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FUEL CELL SEALANT COMPOUNDS

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John F. McCarthy
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Joseph S. Jorczak
Thiokol Corporation

September 1952

WRIGHT AIR DEVELOPMENT CENTER

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Materials Laboratory
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Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report was prepared by the Thiokol Corporation under Contract AF-33(038)-30523, Research and Development Order No. R601-298 SR-79. It represents the results of work performed from 13 July 1951 to 13 July 1952, under the foregoing contract. Capt. C. W. Douglass, project engineer for the Materials Laboratory, Directorate of Research, Wright Air Development Center, administered this contract for the Air Force. At the Thiokol Corporation the work was directed by J. S. Jorczak, manager of the Technical Service Department, and E. M. Fettes, manager of the Research and Development Department; the group leaders conducting the project were E. H. Sorg and J. F. McCarthy.

ABSTRACT

This work was undertaken by the Thiokol Corporation to develop integral fuel tank sealant compounds with improved low and high temperature properties, increased toughness and adhesion, and better resistance to jet fuels.

Experimental integral fuel tank sealant compounds were prepared in two-package mixes from hexamethylene dichloride/triglycol dichloride/formal and pentamethylene dichloride/formal polymers. Compared to a 'Thiokol' LP-2 base sealant, these experimental compounds displayed improved low temperature properties, equivalent toughness and adhesion to aluminum, somewhat better resistance to heat aging at 212°F, and slightly poorer resistance to swell in aromatic fuels.

Compounding studies with 'Thiokol' LP-2 yielded formulations with improved adhesion properties and heat aging resistance.

Development work on clear sealant compounds disclosed the possibility of preparing sealants of this type from combinations of epoxide resins and 'Thiokol' liquid polymers; however, considerably more investigation of this aspect is required.

PUBLICATION REVIEW

Manuscript Copy of this report has been reviewed and found satisfactory for publication.

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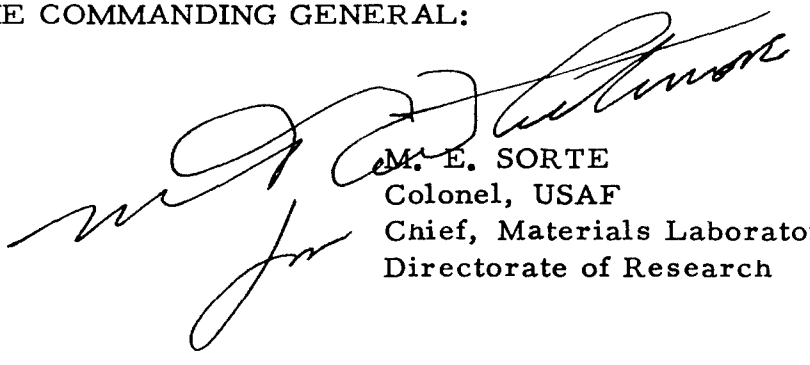

M. E. SORTE
Colonel, USAF
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TABLE OF CONTENTS

TABLE OF CONTENTS (Contd.)

TABLE OF CONTENTS (Contd.)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Contd.)

SUMMARY

I. DEVELOPMENT OF POLYMERS FOR IMPROVED PROPERTIES

A. VARIATIONS IN FORMAL (LP-2 TYPE) POLYMERS

1. Effect of Varying Rank

A series of polymers prepared with 98 mole % of formal and 2 mole % of trichloropropane (TCP) as the crosslinking agent and with variation in polysulfide rank from 1.60 to 2.25 was investigated. Within the range of 1.60 to 2.25, the effect of polymer rank on resistance to volume change in fuels and the low temperature flexibility was of no significance. The high rank polymer was somewhat tougher but 'shorter' and had slightly better resistance to compression set at low temperature. In general, the effects of heat aging appeared to be independent of polymer rank within the foregoing ranges.

2. Effect of Various Crosslinking Agents

Five different series of formal polymers crosslinked with varying amounts of the following compounds were prepared and evaluated to determine the effects on polymer properties. These polymers were prepared with a rank of 2.25 and the amount of crosslinking agent was varied from 0.5 to 2.0 mole %:

1. Trichloropropane (TCP)
2. Tetrachloropropyl formal (TCF)
3. Tetrachloroethoxy-ethane (TCE)
4. Tris(2-chloroethyl) orthoformate
5. Dichloroethyl chloroacetal

Trichloropropane and tetrachloropropyl formal were the best crosslinking agents. With trichloropropane, the low temperature flexibility of heat aged and unaged polymers was independent of the amount of crosslinking agent. The polymer crosslinked with 2 mole % of TCP was more resistant to compression set than those with smaller amounts of reagent. An increase in amount of TCP crosslinking reduced the polymer toughness before and after heat aging.

With tetrachloropropyl formal, polymer toughness, hardness, low temperature flexibility and resistance to volume change in fuels were practically independent of the extent of crosslinking. Heat aging produced no appreciable effect on any of these crosslinked polymers. The polymers crosslinked with this material possessed higher ultimate elongation, poorer resistance to temperatures and in general somewhat better resistance to heat aging than comparable polymers crosslinked with trichloropropane.

Tetrachloroethoxy-ethane was not nearly as satisfactory as trichloropropane or tetrachloropropyl formal for crosslinking. The use of tris(2-chloroethyl) orthoformate as a crosslinking agent appeared to inhibit cure of the polymer. Although the evaluation data indicated that dichloroethyl chloroacetal was not very effective as a crosslinking agent, additional work with this material is required before a sound analysis of its value can be made.

B. PROPERTIES OF COPOLYMERS CONTAINING FORMAL AND VARIOUS MONOM

Studies were conducted on ten different series of formal copolymers to determine the effects of variations in structure on polymer properties. Aside from one pentamethylene dichloride/formal copolymer prepared with a rank of 2.00 and 4 mole % of trichloropropane, these copolymers were all crosslinked with 2 mole % of trichloropropane and had a rank of 2.25; the amount of comonomer varied from 10 to 55 mole %. The following copolymers were studied:

1. Pentamethylene dichloride/formal
2. Hexamethylene dichloride/formal
3. Ethylene dichloride/formal
4. α,α'-Dibromosuccinic acid/formal
5. Glycerol-α,β-dichlorohydrin/formal
6. Dichlorodiethyl ether/formal
7. o-Xylylene dichloride/formal
8. N-Methyl dichlorodiethylamine/formal
9. Bis(2-chloroethyl) amine/formal
10. Dichloropropionitrile/formal

From the standpoint of improved low temperature properties, the pentamethylene dichloride and hexamethylene dichloride/formal copolymers were the most promising for integral fuel cell sealant compounds. All of the other copolymers possessed low temperature flexibilities that were comparable or poorer than those of the formal (LP-2 type) control. As determined by torsional stiffness, tension-retraction and low temperature stress-strain tests, the pentamethylene copolymers displayed a marked improvement over the formal polymer in low temperature properties.

A 54.5/43.5 mole % hexamethylene dichloride/formal copolymer gave a tougher rubber than any of the pentamethylene copolymers and the formal control. Also, it displayed improved low temperature torsional stiffness properties over the formal polymer and showed outstanding resistance to heat aging. However, the use of this copolymer presented compounding difficulties since it was a solid at room temperature. Further, the pentamethylene and hexamethylene dichloride copolymers were less resistant to volume change in fuels than the formal control.

The N-methyl dichlorodiethylamine/formal copolymers exhibited promis-

ing heat aging and toughness properties in conjunction with low temperature properties that were equivalent to those of the formal control. Also, its resistance to volume change in SR-6 fuel was better than that of the formal polymer.

The glycerol-α,β-dichlorohydrin/formal copolymer displayed improved resistance to volume change in aromatic fuel in comparison to the formal polymer.

Somewhat improved resistance to volume change in SR-6 fuel was observed with the o-xylylene dichloride/formal copolymers in comparison to the formal control. However, these copolymers possessed considerably poorer low temperature properties than the control.

None of the variations in polymer structure resulted in improved adhesion to aluminum over the formal control when tested in the standard evaluation formulation. However, good adhesion to aluminum was obtained with the copolymers when small quantities of adhesion additives were incorporated in the test formulation.

C. PROPERTIES OF TERPOLYMERS CONTAINING FORMAL AND VARIOUS MONOMERS

The following terpolymers were prepared with the objective of obtaining a polymer possessing a balance of toughness, good low temperature characteristics, fuel resistance, heat aging resistance and good processibility.

1. 50/25/23/2 mole % hexamethylene dichloride/triglycol dichloride/formal/trichloropropane

2. 21/21/56/2 mole % hexamethylene dichloride/pentamethylene dichloride/formal/trichloropropane

The hexamethylene/triglycol/formal terpolymer showed much promise for use in integral fuel cell sealant compounds with superior low temperature properties and resistance to heat aging. Because of its good high temperature resistance, this terpolymer possesses good possibilities for the preparation of integral engine oil tank sealant compounds. From an over-all viewpoint it may be superior to the pentamethylene/formal copolymer for sealant materials.

With the hexamethylene/pentamethylene/formal terpolymer, a rubber of improved low temperature properties, and better toughness was obtained but the fuel resistance was inferior to that of the formal control. This terpolymer showed some advantage over the triglycol terpolymer in toughness and resistance to SR-6 fuel.

II. DEVELOPMENT OF COMPOUNDING AND CURING METHODS

A. DEVELOPMENT OF HEAT AGING RESISTANCE IN PENTAMETHYLENE DICHLORIDE/FORMAL COPOLYMERS

Since the pentamethylene/formal copolymers displayed promise with respect to improved low temperature properties but had poor apparent resistance to aging at 212°F, studies were conducted to determine whether the poor resistance to heat aging was an inherent property or resulted from factors connected with preparation and/or compounding. The investigation disclosed that the pentamethylene/formal copolymers were inherently no more volatile at 212°F than the formal liquid polymer. The decrease in weight and volume and increase in hardness of thiol-terminated polysulfide liquid polymer rubbers during heat aging was a function of the type of curing agent and compounding materials and of the viscosity of the polymer. It was observed that the use of the lead stearate-lead peroxide curing system in the standard formulation was primarily responsible for the poor resistance of the pentamethylene copolymers to aging at 212°F.

During the conversion reaction of thiol-terminated liquid polysulfide polymers with lead peroxide, -R-S-Pb-S-R- segments are probably formed in the polymer chains; these segments can yield relatively volatile cyclic disulfide ring compounds during aging at 212°F. Further, the seven-membered pentamethylene disulfide cyclic compound was the major product obtained by the dry distillation of a pentamethylene/formal copolymer cured with lead peroxide. This cyclic compound is more easily formed than the nine membered formal disulfide cyclic compound which is produced during the heat aging of formal polymer cured with lead peroxide and accounts for the poorer resistance of the copolymer to aging at 212°F.

Both the pentamethylene/formal copolymer and the formal polymer possessed excellent resistance to decrease in weight and volume and increase in hardness during aging at 212°F when cured with a pure oxidizing mechanism such as the p-quinonedioxime-diphenylguanidine system. However, since the latter system did not cure liquid polymer compounds within 24 hours at 77°F it was necessary to develop a new curing mechanism for the pentamethylene copolymer.

B. ADDITIVES AND CURING AGENTS

A number of studies were conducted with 'Thiokol' LP-2 liquid polymer to develop a room temperature cure that would produce rubbers with good resistance to aging at 212°F. The following systems gave good cures within 24 hours at 77°F and the rubbers possessed very good resistance to heat aging:

1. Lead stearate/lead peroxide/sulfur/maleic anhydride
2. p-Quinonedioxime/triethanolamine/sulfur

The compression set of the rubber prepared from the standard 'Thiokol' LP-2 control formulation at 158°F was greatly improved by the incorporation of sulfur, alone or in conjunction with maleic anhydride, an adhesion additive. Sulfur alone did not affect the compression set at -40°F, but gave an improvement in this property when used with the adhesion additive.

Coatings prepared from combinations of a polyvinyl chloride type latex, Geon Latex No. 652, and softened WD-2 latex were evaluated for toughness and adhesion to aluminum. The polyvinyl chloride type polymer did not improve the toughness or the adhesion properties of the WD-2.

III. DEVELOPMENT OF CLEAR SEALANT COMPOUNDS

Combinations of 'Thiokol' liquid polymers with epoxide type polymers were investigated for the purpose of developing clear sealant compounds. Aromatic amines were used as curing agents in an attempt to obtain room temperature cures, but more than 24 hours was required to obtain full cures. The best compounds displayed good resistance to jet fuels, good tensile and tear strengths, poor elongation and poor low temperature properties. The results obtained thus far indicate that with the proper combination of types of 'Thiokol' liquid polymers and epoxides, this approach should yield a clear tough sealant compound with the necessary requirements. Some studies were also made with LP-2 and cumene hydroperoxide to develop a satisfactory curing mechanism and material for a clear sealant compound, but satisfactory cures were not obtained.

IV. PROPERTIES OF EXPERIMENTAL POLYMER SEALANT COMPOUNDS

Practical two package mix integral fuel cell sealant compounds were prepared from the hexamethylene dichloride/triglycol dichloride/formal and the pentamethylene dichloride/formal experimental polymers and 'Thiokol' LP-2. Compared to the 'Thiokol' LP-2 sealant material, the experimental polymer sealant compounds possessed equivalent toughness, improved low temperature properties, equivalent adhesion to aluminum, as good resistance to heat aging and somewhat poorer resistance to swell in Type III fuel (similar to SR-6). The terpolymer sealant compound was particularly outstanding because of its excellent low temperature properties.

Both of the experimental polymer sealant compounds passed the requirements of Military Specification, Mil-S-5043A(Aer), tests to which they were subjected.

From an over-all viewpoint, the hexamethylene/triglycol/formal terpolymer may be more suitable than the pentamethylene/formal copolymer.

If the resistance of the terpolymer to Type III fuel could be improved, this terpolymer should be considerably better than 'Thiokol' LP-2 for the preparation of sealant compounds.

INTRODUCTION

This report deals with the work performed by the Thiokol Corporation from 13 July, 1951 to 13 July, 1952 under Contract No. AF-33(038)-30523. The investigation was undertaken to develop improved integral fuel cell sealant compounds based on polysulfide polymers. The major improvements desired in these compounds were as follows:

a. Increased toughness
b. Better low temperature properties
c. Improved adhesion
d. Greater resistance to elevated temperature
e. Resistance to jet fuels

Two approaches were followed in attacking this problem, namely, (a) an investigation of the effect of polymer structure and (b) the effects of additives and compounding ingredients on 'Thiokol' LP-2 and promising new polymers.

In this report, an account of the preparation and evaluation of the new polymers is given. Compounding and curing studies that were conducted are also described. Results of the evaluation of two new promising sealant compounds that were submitted to the Air Materiel Command are included.

The preparation methods used for the polymers described in this report are presented in Appendix A; evaluation procedures are given in Appendix B; a glossary of terms that require definition is given in Appendix C.

I. DEVELOPMENT OF POLYMERS TO YIELD THE MOST DESIRABLE PROPERTIES

A. INTRODUCTION

This aspect of the program dealt with the preparation and evaluation of liquid polysulfide polymers with structures that would be inherently conducive to good properties in fuel tank sealant compounds. To attain this end, the following general classes of polymer systems were investigated:

a. Formal (LP-2 type) polymers that were prepared with different ranks and various types and amounts of crosslinking agents.

b. New copolymers of formal and various monomers with structures that were conducive to good inherent properties.

c. Terpolymers of formal in combinations with two other monomers which together would provide a good balance of desirable properties.

The liquid polymers were prepared on a laboratory scale by previously developed techniques described in Appendix A. Thus, in some cases, only small samples were available for evaluation and exhaustive tests were not conducted.

The polymers were for the most part compounded by the following standard evaluation recipe:

Ingredients	Parts
Experimental polymer	100
Zinc sulfide (ZS-800)	50
Lead stearate	1.4
Lead peroxide	7.5

The objective in the evaluation of these polymers was to determine by preliminary screening the structures that yielded better physical properties than those developed by 'Thiokol' LP-2 (formal polymer). Special emphasis was given to such properties as low temperature performance, toughness, heat aging and adhesion to aluminum. Since the foregoing recipe was not designed to develop adhesive properties, this quality was imparted to polymers that showed promise in other respects by incorporation of special adhesion additives in the recipe. The methods used to test the polymers are fully described in Appendix B. Where applicable, either ASTM or military specification tests were employed.

B. VARIATIONS IN FORMAL (LP-2 TYPE) POLYMERS

1. Effect of Variations in Rank

Work was undertaken to determine the optimum rank, (the average number of sulfur atoms linking the hydrocarbon polymer segments) for liquid polymers to be used in sealant compounds. Previous work had yielded some evidence that 'Thiokol' crude polymers with lower ranks tended to display better low temperature flexibility. However, the applicability of this observation to liquid polymers was unknown. Therefore, four formal liquid polymers containing 2 mole % of trichloropropane as a crosslinking agent and varying in rank from 1.60 to 2.25 were prepared and evaluated.

From the data in Table 1, it appears that variation in rank of the polysulfide from 1.60 to 2.25 did not significantly affect the low temperature torsional stiffness properties of the polymer. However, the lower rank polymers retracted somewhat more slowly than did those of higher rank, as shown by the temperature differential between the TR10 and TR70 values. Increase in rank of the polysulfide increased the hardness, 300% moduli and ultimate tensile strengths of the unaged samples according to a definite trend and resulted in lower ultimate elongations for both the heat aged and unaged samples (see Figure 1).

The higher rank polymers possessed somewhat better compression set resistance at low temperatures. With the possible exception of the polymer with a rank of 1.60, which was slightly less resistant to SR-6 fuel, all of the polymers displayed comparable volume changes in SR-6, SR-10 and JP-3A fuels. All of the polymers degraded somewhat after immersion for one day in JP-3A fuel at room temperature. The adhesion properties of these polymers to aluminum were very poor when tested in the control formulation which, however, was not specifically designed for the development of good adhesion properties.

From an over-all point of view, there appears to be no apparent advantage in utilizing polymers with a rank lower than 2.25.

2. Effect of Variations in Type and Amount of Crosslinking Agents

a. Introduction

Since the curatives used for 'Thiokol' polysulfide polymers result in linkages primarily at the end terminals of the polymer chains and in negligible crosslinking, it is desirable to use some type of agent to build branching or crosslinking points into the polymer chains during preparation. For 'Thiokol' LP-2, a trifunctional chlorine compound, trichloropropane in a concentration of 2 mole %, is used. To determine whether this was the optimum quantity of agent and whether any gain could result from the use of other tri- and tetrafunctional chlorine compounds, different types of crosslinking agents in various concentrations were used.

b. Trichloropropane

The effect of varying the amount of trichloropropane (TCP) crosslinking agent in formal liquid polymer from 0.5 to 2.0 mole % was investigated. According to the data in Table 2, an increase in the amount of TCP from 0.5 to 2.0 mole% reduced the ultimate elongation of the polymer. In addition, the ultimate tensile strength of the polymer decreased somewhat with an increase in the amount of crosslinking agent. The low temperature torsional stiffness properties were not affected by varying the amount of TCP within this range. As indicated by the tension-retraction data (TR10-TR70 values), the polymers prepared with 0.5 and 1.0 mole % of TCP retracted more slowly than did the polymers with greater amounts of TCP. The resistance to compression set improved with increasing amounts of crosslinking agent. The polymers prepared with 1.5 and 2.0 mole % of TCP were more resistant to volume change in SR-6 fuel, but all of the polymers were comparable in SR-10 and JP-3A fuels. All of these polymers degraded slightly in JP-3A fuel. The adhesion of the 0.5 mole % polymer to aluminum was very poor; however, the formulation employed was not specifically designed for adhesion.

Heat aging appeared to lower the ultimate tensile strength and elongation of the polymers with 1.5 and 2.0 mole % of TCP but did not appreciably affect those crosslinked with 0.5 and 1.0 mole % of TCP. The low temperature torsional stiffness of these polymers was not changed by heat aging.

Since the liquid polymers with low amounts of crosslinking agent possessed higher tensile strengths and elongations, these polymers will be investigated further. Such properties are considered to be of great value in sealant compounds.

c. Tetrachloropropyl Formal

Theoretically, a greater degree of toughness should be obtained in polymers containing a tetrafunctional rather than a trifunctional crosslinking agent such as trichloropropane. Therefore, formal liquid polymers of rank 2.25 containing 1.0, 1.5 and 2.0 mole % of tetrachloropropyl formal (TCF), a tetrafunctional crosslinking agent, were prepared.

The data in Table 3 reveal that a variation in the amount of TCF from 1.0 to 2.0 mole % did not significantly alter the hardness, ultimate tensile strength and elongation, low temperature torsional stiffness and resistance to volume change of the formal polymers. Slight degradation of all of these polymers occured after immersion for one day in JP-3A fuel. The TR10-TR70 differential values indicated that the polymer containing 1.0% of TCF retracted more slowly than did the one with 1.5%. Heat aging did not appreciably

affect the hardness, elongation and low temperature torsional stiffness of these polymers. The polymer containing 2.0 mole % of TCF had the best compression set at 158° and -20°F. In comparison with the polymers prepared with the same amounts of TCP as the crosslinking agent, these polymers possessed higher ultimate elongation, slightly poorer low temperature torsional properties, poorer resistance to compression set at low temperatures and appeared to be somewhat less resistant to volume change in SR-6 and SR-10 fuels.

d. Tetrachloroethoxy-Ethane

A series of liquid formal polymers was prepared with 0.5, 1.0, 1.5 and 2 mole % of tetrachloroethoxy-ethane (TCE) as the crosslinking agent to compare its effects with those of trichloropropane and tetrachloropropyl formal.

In the standard evaluation formulation these polymers produced rubbers which were very thermoplastic. This could not be attributed to low molecular weight and hence insufficient amounts of curing agent, as the viscosities of these polymers, with the exception of the 0.5 mole % TCE polymer, indicated that they were in the LP-2 molecular weight range. When 0.25 part of sulfur per 100 parts of polymer were incorporated in the formulation, the rubbers were not thermoplastic at 212°F. This indicated that tetrachloroethoxy-ethane was not an effective crosslinking agent.

Although the polymers compounded without sulfur seemed to be deficient in crosslinking, their physical properties were determined for purposes of comparison with the trichloropropane- and tetrachloropropyl formal-crosslinked polymers. According to the data in Table 4, the physical properties of all the tetrachloroethoxy-ethane crosslinked polymers were extremely poor. The samples flowed during aging at 212°F and the compression set plugs flowed while cold. After heat aging, all four compounds were extremely 'short'.

The data obtained for the polymers cured with 0.25 part of sulfur in the formulation are presented in Table 5. The physical properties of the polymers containing 1, 1.5 and 2 mole % of TCE were very poor. These polymers became quite brittle after aging for 72 hours at 212°F. In addition, the low temperature torsional stiffness properties became slightly poorer with an increase in the amount of TCE. It is apparent that tetrachloroethoxy-ethane is not as satisfactory as trichloropropane and tetrachloropropyl formal for crosslinking.

e. Tris(2-chloroethyl) Orthoformate

Four liquid formal polymers containing 0.5, 1.0, 1.5 and 2.0

mole % of tris(2-chloroethyl) orthoformate were prepared to determine the suitability of this material as a crosslinking agent. The properties of the unconverted polymers are shown in Table 6. It was impossible to cure these polymers at 77°F even with twice the amount of lead peroxide specified in the evaluation formulation and 0.25 part of sulfur. Also, cures were not obtained with this formulation after heating for 24 hours at 158°F, despite the fact that all of the LP-2 control formulations cured normally.

f. Dichloroethyl Chloroacetal

Formal polymers crosslinked with 0.5, 1.0, 1.5 and 2 mole % of dichloroethyl chloroacetal were prepared. The cake hardness of the polymers prior to splitting and the viscosity of the liquid polymers were comparatively low. Considerable difficulty was encountered in the toughening of these polymers. Therefore, they were given only a superficial evaluation.

Although twice the regular amount of lead peroxide was used in the test formulations, these polymers appeared to be somewhat undercured. According to the data in Table 7, the hardness and tensile strength of these polymers were in the same category and were comparatively low. The ultimate elongations of these polymers were quite high and in the same range. Dichloroethyl chloroacetal was not as satisfactory as trichloropropane and tetrachloropropyl formal for crosslinking.

C. COPOLYMERS OF FORMAL IN COMBINATION WITH VARIOUS MONOMERS

1. Introduction

Copolymers of formal with various comonomers were prepared with a view to achieving polymer structures that would upgrade the properties of formal polymer (LP-2 type). Thus, the various comonomers were employed to effect the following improvements:

a. Improved low temperature performance - pentamethylene and hexamethylene dichloride.

b. Improved toughness - dichlorodiethyl ether, glycerol-α, β-dichlorohydrin, α, α'-dibromosuccinic acid, ethylene dichloride, dichloropropionitrile, O-xylylene dichloride.

c. Improved adhestion--α, α'-dibromosuccinic acid, glycerol-α, β-dichlorohydrin, bis(2-chloroethyl)amine, dichloropropionitrile.

The copolymers were prepared with 38 mole % of formal and upwards, 10 to 60 mole % of the various comonomers and 2 mole % of a crosslinking agent.

2. Pentamethylene Dichloride/Formal Copolymers

Liquid copolymers of approximately 60/40 pentamethylene dichloride/formal with TCP as the crosslinking agent were prepared. These copolymers were evaluated both in the standard evaluation formulation and in one designed more specifically to withstand heat aging.

The results in Table 8 indicate that these copolymers showed a substantial improvement over the formal control in low temperature torsional flexibility and tension-retraction properties. The absolute torsional modulus of 5,000 lb/sq in. for these copolymers was attained at a temperature that was approximately 15°F lower than with the control polymer, see Figure 2. In addition, according to the tension-retraction data and the curves in Figure 3, these copolymers reached 10 and 30% retraction at a temperature about 15°F lower than the formal control.

To evaluate further the low temperature properties, the stress-strain relationships of the 2 mole % TCP copolymer and the formal control polymer were studied at 80, 0, -30, -50, -60, -70 and -80°F. Curves representing the relationship between ultimate tensile strength, ultimate elongation and modulus of stretch at failure and temperature were plotted. The data in Table 9 and the curves in Figure 4 show that the pentamethylene copolymer possessed somewhat higher tensile strength in the temperature range of 0 to -60°F, but in the temperature range of -60 to -80°F it had considerably lower tensile strength than the control polymer. From Figure 5 it is apparent that the copolymer maintained substantially higher ultimate elongation over the entire temperature range than did the control polymer. At -70°F, the copolymer possessed a higher ultimate elongation than that of the control at -50°F. High elongation over a wide temperature range is a requirement for integral fuel cell sealant compounds. The relationship between ultimate tensile strength and elongation, modulus of stretch at failure, throughout the temperature range is illustrated by the curves in Figure 6. The copolymer and control were comparable in this relationship over the temperature range of 80° to -50°F, but at temperatures lower than -50°F the copolymer possessed a much lower modulus of stretch at failure. A low modulus of stretch at failure at low temperatures is thought to be an essential property for sealant materials. It should be pointed out that at temperatures between 80° and 0°F the curves are hypothetical.

The tensile and tear strength and elongation data in Table 8 indicate that the unaged sample with 2% of TCP was comparable to the control in toughness. In the standard evaluation formulation, heat aging drastically degraded the physical properties of both copolymers and the test samples decreased considerably in volume and weight. After heat aging, the specimens cracked when folded 180°. However, in a compound designed specifically for

the purpose (Compound No. 34367-1), the copolymer exhibited excellent heat aging characteristics.

The pentamethylene copolymers were less resistant to volume change in SR-6, SR-10 and JP-3A fuels than the formal control polymer. The adhesion of these copolymers to aluminum was very poor as evaluated in the test formulation. However, incorporation of small amounts of additives in the formulation to impart adhesion properties gave compounds with very good room temperature adhesion to aluminum.

3. Hexamethylene Dichloride/Formal Copolymers

To study the effect of hexamethylene dichloride on low temperature characteristics, a copolymer was prepared with 60 mole % of hexamethylene, 38 mole % of formal and 2 mole % of TCP by the standard procedure. Since the 'as-received' copolymer was a hard waxy solid, it was redistributed with 10% (by weight) of ZL-109 to facilitate compounding.

The data in Table 10 reveal that this copolymer showed a definite improvement in low temperature torsional stiffness. In comparison to the formal control, it had an absolute torsional modulus of 5000 lb/sq in. at a temperature that was 8°F lower (see Figure 2). According to the tension-retraction data in Table 10 and the curves in Figure 3, the hexamethylene copolymer attained 10 and 30% retraction at temperatures approximately 25°F lower than the control polymer and about 10°F lower than the 60 mole % pentamethylene copolymers. However, the copolymer acquired a permanent set at 55% retraction for the remainder of the test. The tensile and tear strengths and elongation indicate that this copolymer possessed improved toughness over the formal control. Its physical and low temperature properties were not degraded by heat aging and unlike the pentamethylene copolymers, a very small weight loss and volume change occurred in this test. The resistance of this copolymer to volume change in SR-6 and SR-10 fuels was somewhat poorer than that of the formal control. In JP-3A fuel, hexamethylene was considerably worse than the control. As evaluated in the test formulation, the adhesion of this copolymer to aluminum was very poor. When tested in an adhesive formulation, good but spotty adhesion was obtained and the compound was crumbly.

4. Ethylene Dichloride/Formal Copolymers

Liquid copolymers of ethylene dichloride/formal containing 10, 20 and 30 mole % of ethylene dichloride were prepared and evaluated.

According to the data in Table 11, the copolymers containing 10, 20 and 30 mole % of ethylene dichloride possessed very poor ultimate tensile strength and elongation and were inferior in these properties to the formal control. The 20 and 30 mole % copolymers were poorer than the 10 mole % copolymer in torsional stiffness. The data indicated that all of these copolymers were less resistant to volume change in SR-10 fuel than the formal control of

equivalent rank and crosslinking. After immersion for one week in JP-3A fuel, none of these copolymers showed any indications of degradation; however, they were attacked after a period of one month. The adhesion of these copolymers to aluminum was very poor. Heat aging did not significantly affect the properties of these copolymers.

The stress-strain relationship of the three copolymers was determined at 80, -30, -50, -60 and -70°F to obtain preliminary data with the low temperature test procedure. From the data in Table 12 and the curves in Figure 7 it is apparent that the tensile strength of the three copolymers remained fairly constant until a critical temperature was reached; the tensile strength then increased very rapidly with a small change in temperature. This occurred at about -50°F for the 10 and 20 mole % ethylene dichloride copolymers and the formal control and about -30°F for the 30 mole % copolymer. The elongation of the three copolymers decreased very rapidly with a small drop in temperature below -50°F. The formal control showed a more gradual decrease in elongation with temperature. Tests were not conducted at temperatures between 80° and -30°F with the copolymer compounds; these portions of the curves are hypothetical.

5. Dibromosuccinic Acid/Formal Copolymers

A series of α, α'-dibromosuccinic acid/formal copolymers was prepared with 10, 20 and 30 mole % of the acid to determine the effect on toughness and adhesion properties. The copolymers were prepared by the standard procedure except that the acid was added intermittently as a dry powder while the formal/TCP mixture was being fed into the reaction flask.

The data in Table 13 show that the 10 mole % α, α'-dibromosuccinic acid/formal copolymer was superior to the 20 and 30 mole % copolymers with respect to toughness, as measured by tensile strength and elongation. All three copolymers showed a marked reduction in toughness after heat aging. Except for this fact, the 10 mole % copolymer would be promising for improved toughness. These copolymers and the formal control polymer were comparable in low temperature flexibility, as determined by the absolute torsional moduli. The tension-retraction data show the 20 mole % copolymer to possess some advantage over the control polymer in this property. According to the TR10-TR70 values, these copolymers retracted more rapidly than did the formal control. The three copolymers and the formal control displayed comparable resistance to volume change in SR-6, SR-10 and JP-3A fuels. They were all attacked to a minor extent by JP-3A fuel. Copolymerization of formal with α, α'-dibromosuccinic acid did not improve the adhesion to aluminum.

6. Glycerol-α, β-Dichlorohydrin/Formal Copolymers

Two series of copolymers were prepared to study the effect of glycerol-α, β-dichlorohydrin on the toughness and adhesion characteristics of the formal polymer. The copolymers prepared with 10, 20 and 30 mole % of glycerol-α, β-dichlorohydrin cured partially during compounding on the paint mill.

Therefore, they were redistributed by dilution with 10%, by weight, of 'Thiokol' ZL-109 followed by heating overnight at 212°F. A second series containing 20 and 30 mole % of the comonomer and of lower viscosity than the first series was made and evaluated to determine the specific effect of redistribution on the properties.

From the data in Table 14, glycerol-α,β-dichlorohydrin, in the range employed reduced considerably the toughness of the formal polymer considerably, as judged by tensile and tear strength and elongation. All of these copolymers displayed poor toughness compared to the formal control; the 30 mole % copolymer was the weakest and 'shortest'.

Redistribution of the copolymers with ZL-109 did not significantly alter the toughness properties. The redistributed copolymers showed no advantage over the control polymer with respect to compression set. According to the absolute moduli data, the three redistributed copolymers and the control polymer were comparable in low temperature torsional stiffness. Because of their low ultimate elongations, tension-retraction results at 100% elongation could not be obtained on most of these copolymers. However, the 10 mole % redistributed copolymer was somewhat better than the control in this property. The low temperature torsional flexibilities of the 20 and 30 mole % copolymers that were not redistributed with ZL-109 were slightly poorer than those of the corresponding redistributed copolymers. The copolymers that were not redistributed possessed better resistance to volume change in SR-6 fuel than did the formal control.

The adhesion of all of these copolymers to aluminum was very poor when evaluated in the standard test formulation; it was no better than that of the control. However, good adhesion to aluminum was obtained when 0.25 part each of maleic anhydride and furoic acid per 100 parts copolymer (20 mole % glycerol-α,β-dichlorohydrin not redistributed with ZL-109) were added to the standard formulation.

7. Dichlorodiethyl Ether/Formal Copolymers

This series of copolymers was prepared with 10, 20 and 30 mole % of dichlorodiethyl ether to study the effects of this type of structure on toughness.

On reaction with sodium polysulfide solution, dichlorodiethyl ether yields a polymer and a byproduct, thioxane, which must be removed by steam distillation. Therefore, these copolymers were prepared by redistribution of a 98/2 ether/TCP latex with a 98/2 formal/TCP latex and subsequent splitting to liquid polymers.

According to the data in Table 15, copolymers of dichlorodiethyl ether with formal possessed appreciably lower toughness compared to the formal control, as indicated by the lower tensile and tear strength and elongation.

All of these copolymers were poor in these properties. In addition, their resistance to heat aging was extremely poor. The test specimens shrank considerably during heat aging and cracked when flexed 180° after the 72-hour aging period. The hardness increased greatly and the physical properties were markedly degraded by heat aging.

Generally, these copolymers were inferior to the formal control in compression set. The non-heat aged samples of these copolymers were comparable in low temperature torsional flexibility and were equivalent to the control polymer in this property. Since the heat aged samples cracked on stretching they were not evaluated for low temperature torsional stiffness. The tension-retraction data show that these copolymers displayed no significant improvement over the control in this property. Resistance to volume change of these copolymers in SR-6 fuel was in the same range as that of the formal control but was not as good as that of the formal control in SR-10 fuel. The copolymers started to degrade after two weeks of immersion in JP-3A fuel. In the standard evaluation formulation, these copolymers did not adhere to aluminum. However, when 1 part of furoic acid and 0.5 part of BRR-18794 per 100 parts of copolymer were incorporated into the formulation, very good adhesion was obtained.

8. o-Xylylene Dichloride/Formal Copolymers

This series of copolymers was prepared by the standard procedure with 10 and 20 mole % of o-xylylene dichloride to study the effects of this structure on polymer toughness.

The data in Table 16 show that copolymerization of these amounts of o-xylylene dichloride with formal produced copolymers that possessed no significant advantage over the formal control with regard to toughness qualities, as determined from tensile and tear strengths and elongation of the unaged samples. Both copolymers possessed somewhat better resistance to heat aging than did the control polymer, as judged by a comparison of the physical properties of the unaged and heat aged samples. As indicated by the low temperature torsional stiffness and tension-retraction tests, these copolymers had considerably poorer low temperature properties than did the control. The 20 mole % copolymer was the poorest in these low temperature properties. This indicates that aromatic structures are not desirable for good low temperature properties. The resistance of the copolymers to volume change in SR-6 fuel was better than that of the formal control; in SR-10 and JP-3A fuels, comparable solvent resistance was displayed.

9. N-Methyl Dichlorodiethylamine/Formal Copolymers

Two copolymers containing 10 and 20 mole % of N-methyl dichlorodiethylamine were made to study the effect of introducing this structure into the formal polymer on its low temperature and adhesion properties.

Because of the vesicant action of the N-methyl dichlorodiethylamine, it was not desirable to use this material in the form of the free compound.

Consequently, the monomer was prepared and used in the form of the hydrochloride salt which is somewhat safer to handle. The hydrochloride salt was dissolved in water and added to the reaction after the formal/TCP mixture had been added. Because of the presence of the hydrochloride, it was necessary to add sufficient sodium hydroxide to the sodium polysulfide to neutralize the hydrochloric acid.

According to the data in Table 17, these copolymers showed promise for improved toughness in comparison with the formal control. The 20 mole % copolymer possessed very high tear strength. As indicated by the effect on the physical properties, the resistance of both copolymers to heat aging was somewhat better than that of the formal control. They had comparable low temperature torsional stiffness and tension-retraction properties and showed no advantage over the formal control in these respects. Their resistance to volume change in SR-6 was better than that of the formal control. In SR-10 and JP-3A fuel, the copolymers displayed comparable solvent resistance to the formal control. As indicated by the results obtained with the 20 mole % N-methyl dichlorodiethylamine copolymer, copolymerization of formal with N-methyl dichlorodiethylamine did not improve the adhesion properties of the polymer to aluminum when tested in the standard formulation. However, excellent adhesion to aluminum was obtained when 0.25 part each of maleic anhydride and furoic acid per 100 parts of copolymer were incorporated in the test compound.

The foregoing results demonstrate the possibilities of making terpolymers of N-methyl dichlorodiethylamine with pentamethylene or hexamethylene dichloride and formal to obtain the best over-all balance of properties for sealant compounds.

10. Bis(2-chloroethyl) Amine/Formal Copolymers

This series of copolymers was prepared with 10 and 20 mole % of bis (2-chloroethyl) amine to determine the effect of this polymer structure on low temperature, toughness and adhesion properties.

Since these copolymers were of low molecular weight, twice the quantity of lead peroxide specified in the control formulation and sulfur were required to obtain satisfactory cures. According to the tensile and tear strengths and elongation data in Table 18, the two copolymers were comparable in toughness and resistance to heat aging. The non-heat aged samples showed no significant advantage over the formal control in toughness characteristics. The apparent resistance of the two copolymers to heat aging was somewhat better than that of the control, but the presence of sulfur in the copolymer compounds may have been responsible for this. These copolymers were generally comparable to the control in low temperature torsional stiffness and tension-retraction properties. Both copolymers were in the same category as the control polymer with respect to volume change in SR-6, SR-10 and JP-3A fuels. Copolymerization of formal with bis(2-chloroethyl) amine did not improve the adhesion properties of the polymer to aluminum when tested in the evaluation formulation. Very good adhesion to aluminum was obtained when 0.25 part each of adhesion

additives maleic anhydride and furoic acid per 100 parts of copolymer were added to the test formulation.

It should be noted that although the bis(2-chloroethyl) amine copolymers were of very low viscosity, they possessed physical properties that were in the same range as those of the formal control.

11. Dichloropropionitrile/Formal Copolymers

Copolymers containing 10 and 20 mole % of dichloropropionitrile were prepared to study the effect of this polymer structure on toughness, adhesion and low temperature properties.

Although the viscosities of these copolymers were in a satisfactory range, twice the standard quantity of lead peroxide was employed in the test formulations in order to obtain acceptable cures. The data in Table 19 show that the physical properties of the unaged copolymers were inferior to those of the formal control. However, the copolymers were more resistant to heat aging at 212°F as indicated by smaller decreases in the weight and volume of the copolymers after 72 hours of aging at 212°F. At 158°F, the dichloropropionitrile copolymers had better compression set resistance than the formal.

Both copolymers had low temperature torsional stiffness and tension-retraction properties that were comparable to those of the formal control. The volume swell of the two copolymers after immersion for one day in SR-6 was equivalent to that of the formal control. However, after immersion for one month the copolymers showed no evidence of extraction. Also, the 20 mole % copolymer did not appear to be attacked by JP-3A fuel. The adhesion characteristics of these copolymers to aluminum were no better than those of the formal polymer when tested in the evaluation formulation without additives.

D. TERPOLYMERS OF FORMAL IN COMBINATION WITH VARIOUS MONOMERS

1. Introduction

Copolymers of hexamethylene or pentamethylene dichloride with formal displayed superior low temperature properties. However, copolymers containing pentamethylent dichloride generally possessed poor heat aging properties. The hexamethylene dichloride/formal copolymer had good low temperature flexibility and much better heat aging resistance, but was a solid at room temperature. To take advantage of the desirable properties resulting from the use of the foregoing monomers and to minimize their defects, the following terpolymers incorporating these monomers were synthesized and evaluated:

a. 50/25/23/2 Hexamethylene dichloride/triglycol dichloride/formal/TCP.

b. 21/21/56/2 Hexamethylene dichloride/pentamethylene dichloride/formal/TCP.

2. Hexamethylene Dichloride/Triglycol Dichloride/Formal Terpolymer

A terpolymer containing 50 mole % of hexamethylene dichloride, 25 mole % of triglycol dichloride, 23 mole % of formal and 2 mole % of TCP was prepared and evaluated.

According to the results in Table 20, this terpolymer appeared very promising for compounding integral fuel cell sealant compounds of improved heat aging and low temperature properties. It was comparable to the 60/38/2 pentamethylene dichloride/formal/TCP copolymer in low temperature torsional stiffness and possessed somewhat better low temperature tension-retraction characteristics (See Figures 9 and 10). The toughness of the terpolymer was somewhat poorer than that of the formal polymer and pentamethylene/formal copolymer compounded in the same formulation. The terpolymer was decidedly better than the pentamethylene/formal copolymer and the formal control in resistance to heat aging at 212°F in the standard lead peroxide test formulation. It decreased only by approximately 2% in weight and volume and the hardness was virtually unchanged after 216 hours aging at 212°F. Its resistance to swelling was not as good as that of the pentamethylene copolymer in SR-6 fuel but was better in SR-10 fuel. The adhesion of the terpolymer to aluminum was no better than that of the formal control when tested in the standard evaluation formulation.

3. Hexamethylene Dichloride/Pentamethylene Dichloride/Formal

A 21/21/56/2 mole % hexamethylene dichloride/pentamethylene dichloride/formal/TCP terpolymer was prepared to determine the effect of this structure on low temperature, toughness and heat and fuel resistance properties. Although this terpolymer was of comparatively low molecular weight, it was evaluated to provide initial information on its behavior.

The data in Table 21 reveal that this terpolymer was comparable to the 60/38/2 penthamethylene dichloride/formal/TCP copolymer and the 50/25/23/2 hexamethylene dichloride/triglycol dichloride/formal/TCP terpolymer in low temperature torsional stiffness characteristics. It was inferior to the triglycol terpolymer in low temperature tension-retraction characteristics. This terpolymer was somewhat tougher than the penthamethylene/formal copolymer and the triglycol terpolymer and possessed considerably better resistance to heat aging than the pentamethylene copolymer. Its resistance to heat aging was poorer than that of the triglycol terpolymer but it was better than that of the formal control. The resistance of this terpolymer to swelling was comparable to that of the pentamethylene copolymer in SR-6 fuel and better than that of the triglycol terpolymer; in SR-10 fuel this terpolymer was better than the pentamethylene copolymer. In the standard evaluation formulation, the hexamethylene/pentamethylene/formal terpolymer did not adhere to aluminum.

This terpolymer system possesses definite promise for use in an integral fuel cell sealant compound with improved low temperature properties, possibly better toughness and satisfactory fuel resistance.

TABLE I

EFFECT OF POLYSULFIDE RANK ON PROPERTIES OF FORMAL POLYMER

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R1	A19437R2	A19437R3	A19437R4
				Formal Control
Formal, mole %	98	98	98	98
Trichloropropane, mole %	2	2	2	2
Rank	1.60	1.80	2.00	2.25
Cake hardness	41	45	47	49
Brookfield viscosity, poises	670	705	985	1400
	Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]			
Compound No.	25961-1 b/c	25961-2 b/c	25961-3 b/c	25961-4 b/c
Shore hardness	37/42	42/43	47/53	47/53
100% Modulus, lb/sq. in.	75/100	100/100	100/150	125/160
300% Modulus, lb/sq. in.	125/210	190/190	290/325	325/--
Tensile strength, lb/sq. in.	325/410	400/325	460/390	540/360
Elongation, %	890/680	780/610	510/360	500/250
Compression set, %				
At 1 hour				
180°F	100	106	92	72
158°F	97	96	96	71
-20°F	32	48	20	18
-40°F	45	49	27	22
Torsional test				
Relative modulus				
T_{5}, -°F	48/50	50/40	50/53	40/52
T_{10}	55/57	56/56	56/57	52/57
T_{50}	64/66	66/65	65/65	63/65
T_{100}	66/70	67/68	66/67	65/66

(Table continued and footnotes on next page).

TABLE 1 (Contd.)

Compound No.	25961-1	25961-2	25961-3	25961-4
Rank	1.60 c/d	1.80 c/d	2.00 c/d	2.25 c/d
Torsional test				
Absolute modulus				
G_{rt}, lb/sq. in.	125/127	123/132	177/241	119/221
$G_{5,000}$, -°F	64/66	66/64	62/62	62/62
$G_{10,000}$,	67/69	69/67	66/66	66/65
$G_{20,000}$	69/72	70/70	67/69	67/68
Tension-retraction				
TR10, -°F	65	65	65	64
TR30	51	55	58	58
TR50	33	40	52	53
TR70	14	22	37	42
TR10-TR70	51	43	28	22
Swelling volume, %				
SR-6 1 Day	18	14	14	14
1 Month	2	2	-2	-2
SR-10 1 Day	1	1	2	0
1 Month	-5	-3	2	-4
JP-3A 1 Day	2[d]	5[d]	5[d]	4[d]
1 Month	5[d]	6[d]	6[d]	8[d]
Adhesion				
After 24-hr. cure	e	e	e	--
After 48-hr. immersion in SR-6	e	e	e	--

a Except where indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Surface of specimen attacked.
e Poor adhesion.

TABLE 2

EFFECT OF AMOUNT OF TRICHLOROPROPANE CROSSLINKING AGENT ON PROPERTIES OF FORMAL POLYMER

(Compounded by Standard Evaluation Recipe, Appendix B.)

Polymer No.	A19441R1	A19441R2	A19441R3	A19437R4
Formal, mole %	99.5	99	98.5	98
Trichloropropane, mole %	0.5	1.0	1.5	2.0
Rank	2.25	2.25	2.25	2.25
Cake hardness	42	43	44	49
Brookfield viscosity, poises	680	725	965	1400
Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]				
Compound No.	25961-5 b/c	25961-6 b/c	25961-7 b/c	25961-4 b/c
Shore hardness	47/52	50/53	50/53	47/53
100% Modulus, lb/sq. in.	100/150	150/160	170/160	125/160
300% Modulus, lb/sq. in.	210/250	325/310	375/--	325/--
Tensile strength, lb/sq. in.	740/675	890/825[d]	680/400	540/360
Elongation, %	880/920	800/750	590/300	500/250
Compression set, %				
At 1 hour				
180°F	99	98	98	72
158°F	96	96	91	71
-20°F	13	22	28	18
-40°F	40	38	32	22
Torsional test				
Relative modulus				
T_5, -°F	48/51	52/50	53/52	40/52
T_{10}	56/56	57/56	58/57	52/57

(Table continued and footnotes on next page.)

TABLE 2 (Contd.)

Compound No.		25961-5	25961-6	25961-7	25961-4
Trichloropropane, mole %		0.5 b/c	1.0 b/c	1.5 b/c	2.0 b/c
Torsional Test					
Relative modulus					
T_{50}, -°F		66/65	65/65	66/65	63/65
T_{100}		67/67	68/68	69/69	65/66
Absolute modulus					
G_{rt}, lb/sq. in.		208/209	214/181	234/256	119/221
$G_{5,000}$, -°F		62/62	62/63	63/61	62/62
$G_{10,000}$		66/65	67/66	66/64	66/65
$G_{20,000}$		68/69	69/69	68/67	67/68
Tension-Retraction					
TR10, -°F		64	65	66	64
TR30		59	60	61	58
TR50		44	50	56	53
TR70		13	24	45	42
TR10-TR70		51	41	21	22
Swelling volume, %					
SR-6	1 Day	11	13	13	14
	1 Month	-16	-12	-6	-2
SR-10	1 Day	0	0	1	0
	1 Month	-2	-5	-5	-4
JP-3A	1 Day	3[e]	3[e]	4[e]	4[e]
	1 Month	4[e]	4[e]	5[e]	8[e]
Adhesion,					
After 24-hr. cure		f	--	--	--
After 48-hr. cure		f	--	--	--

a Except where indicated otherwise, the specimens were unaged.
b Unaged.
c Surface of specimen attacked.
d Surface of test specimen cracked during testing.
e Surface of specimen attacked.
f Poor adhesion.

TABLE 3

EFFECT OF AMOUNT OF TETRACHLOROPROPYL FORMAL CROSSLINKING AGENT ON PROPERTIES OF FORMAL POLYMER

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A19445R2	A19445R3	A19445R4
	Formal Control			
Formal, mole %	98	99	98.5	98
Trichloropropane, mole %	2.0	--	--	--
Tetrachloropropyl formal, mole %	--	1.0	1.5	2.0
Rank	2.25	2.25	2.25	2.25
Cake hardness	49	45	46	49
Brookfield viscosity, poises	1400	445	395	395
	Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]			
Compound No.	25961-4	25971-1	25971-2	25971-3
	b/c	b/c	b/c	b/c
Shore hardness	47/53	43/43	45/47	45/47
100% Modulus, lb/sq in.	125/160	150/150	150/125	160/150
300% Modulus, lb/sq in.	340/300	260/225	275/240	260/250
Tensile strength, lb/sq in.	540/360	525/450	600/510	540/400
Elongation, %	500/250	830/890	880/900	880/880
Compression set, %				
At 1 hour				
180°F	72	100	100	100
158°F	71	98	95	55
-20°F	18	51	70	46
-40°F	22	68	61	66

(Table continued on next page.)

TABLE 3 (Contd.)

Compound No.	25961-4	25971-1	25971-2	25971-3
	b/c	b/c	b/c	b/c
TCF, mole %	--	1.0	1.5	2.0
TCP, mole %	2.0	--	--	--
Torsional Test				
Relative modulus				
T_5, -°F	40/52	49/46	49/48	49/46
T_{10}	52/57	55/54	54/54	53/53
T_{50}	63/65	60/61	62/62	63/60
T_{100}	65/66	63/62	65/63	65/62
Torsional Test				
Absolute modulus				
G_{rt}, lb/sq in.	119/221	142/114	172/137	149/130
G_{5000}, -°F	62/62	61/61	61/61	60/60
$G_{10,000}$	66/65	63/63	63/63	63/62
$G_{20,000}$	67/68	65/65	67/65	65/64
Tension-retraction				
TR 10, -°F	64	65	65	--
TR 30	58	57	60	--
TR 50	53	43	44	--
TR 70	42	14	27	--
TR 10-TR 70	22	51	38	--
Swelling volume, %				
SR-6 1 Day	14	10	11	10
1 Month	-2	-12	-16	-16
SR-10 1 Day	0	5	5	6
1 Month	-4	-12	-24	-11
JP-3A 1 Day	4^d	4^d	4^d	3^d
1 Month	8^d	7^d	3^d	5^d

(Table continued and footnotes on next page)

TABLE 3 (Contd.)

Compound No.	25961-4	25971-1	25971-2	25971-3
TCF, mole %	--	1.0	1.5	2.0
TCP, mole %	2.0	--	--	--
Adhesion				
After 24-hr. cure	--	Poor	--	--
After 48-hr. immersion in SR-6	--	Poor	--	Poor

a Except where indicated otherwise, the specimens were unaged.
b Unaged
c Aged for 72 hours at 212°F.
d Surface of specimen attacked.

TABLE 4

EFFECT OF TETRACHLOROETHOXY-ETHANE CROSSLINKING AGENT ON FORMAL POLYMER

(Compounded by the Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A29533W1	A29533W2	A29533W3	A29533W4
	Formal Control				
Formal, mole %	98	99.5	99	98.5	98
Tetrachloroethoxy-ethane, mole %	--	0.5	1	1.5	2
Trichloropropane, mole %	2	--	--	--	--
Rank	2.25	2.25	2.25	2.25	2.25
Cake hardness	49	42	43	43	50
Brookfield viscosity, poises	1400	280	470	450	480
	Vulcanizate Properties (Cured 24 hr. @ 77°F) [a]				
Compound No.	25961-4	34357-1	34357-2	34357-3	34357-4
	b/c	b/c	b/c,d	b/c,d	b/c,d
Shore hardness	47/53	43/53	48/60	47/55	47/47
100% Modulus, lb/sq. in.	125/160	150/150	150/e	150/--	150/--
300% Modulus, lb/sq. in.	325	--	--	--	--
Tensile strength, lb/sq. in.	540/360	150/240	225	160/175	150/150
Elongation, %	500/250	290/20	150	150/10	110/10
Tear strength, lb/in.	44/53	53/38	21	20/0	19/0
Compression set, %					
At 1 hour					
158°F	71	f	f	f	f
-40°F	22	f	f	f	f

a Except where indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F; samples were thermoplastic and flowed.
d After 72 hours of aging at 212°F, the samples cracked when flexed 180°.
e Test specimen broke during handling.
f Test specimens were unsatisfactory because of cold flow.

TABLE 5

EFFECT OF TETRACHLOROETHOXY-ETHANE CROSSLINKING AGENT ON FORMAL POLYMER

(Compounded by the Standard Evaluation Recipe plus 0.25 Part of Sulfur)

Polymer No.	A19437R4	A29533W1	A29533W2	A29533W3	A29533W4
	Formal Control				
Formal, mole %	98	99.5	99	98.5	98
Tetrachloroethoxy-ethane, mole %	--	0.5	1	1.5	2
Trichloropropane, mole %	2	--	--	--	--
Rank	2.29	2.25	2.25	2.25	2.25
Cake hardness	49	42	43	43	50
Brookfield viscosity, poises	1400	280	470	450	480
	Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]				
Compound No.	25961-4 b/c	34362-1 b/c	34362-2 b/c	34362-3 b/c	34362-4 b/c
Shore hardness	47/53	56/57	57/60	56/58	57/d
100% Modulus, lb/sq. in.	125/160	190/210	225/--	--	--
300% Modulus, lb/sq. in.	325/--	440/410	--	--	--
Tensile strength, lb/sq. in.	540/360	510/725	225/210	150/240	200/--
Elongation, %	500/250	375/620	100/70	70/90	70/--
Tear strength, lb/in.	44/53	62/68	0/18	0/0	0/0
Compression set, %					
At 1 hour					
158°F	71	90	94	93	100
-40°F	22	21	22	18	42
Torsional test					
Relative Modulus					
T_5, -°F	40	54	52	52	48
T_{10}	52	58	55	56	52
T_{50}	63	66	64	62	60
T_{100}	65	68	67	65	63
Absolute Modulus					
G_{rt}, lb/sq. in.	119	237	265	259	238
$G_{5,000}$, -°F	62	62	59	59	57
$G_{10,000}$	66	65	62	62	60
$G_{20,000}$	67	68	65	64	63

a Except where indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Test specimens broke during handling; the stock was very 'short'.

TABLE 6

PROPERTIES OF UNCONVERTED FORMAL POLYMERS CONTAINING TRIS (2-CHLOROETHYL) ORTHOFORMATE CROSSLINKING AGENT[a]

Polymer No.	A29528W1	A29529W1	A29530W2	A29531W3
Formal, mole %	99.5	99	98.5	98
Tris(2-chloroethyl) orthoformate, mole %	0.5	1	1.5	2
Rank	2.25	2.25	2.25	2.25
Cake hardness	42	41	41	40
Brookfield viscosity, poises	510	390	305	350

a Physical tests were not conducted since the polymers could not be cured at 77°F.

TABLE 7

EFFECT OF DICHLOROETHYL CHLOROACETAL CROSSLINKING AGENT ON FORMAL POLYMER

(Compounded by Standard Evaluation Recipe, Appendix B, with Double the Amount of Lead Stearate and Lead Peroxide.)

Polymer No.	A19437R4	A29532W1	A29532W2	A29532W3	A29532W4
	Formal Control				
Formal, mole %	98	99.5	99	98.5	98
Dichloroethyl chloroacetal, mole %	--	0.5	1	1.5	2
Trichloropropane, mole %	2	--	--	--	--
Rank	2.25	2.25	2.25	2.25	2.25
Cake hardness	49	35	36	42	33
Brookfield viscosity, poises	1400	145	175	75	180
	Vulcanizate Properties (Cured 24 hr. @ 77°F)				
Compound No.	25961-4	34379-1	34379-2	34379-3	34379-4
Shore hardness	47	36	37	43	33
100% Modulus, lb/sq in.	125	80	90	110	60
300% Modulus, lb/sq in.	325	140	140	160	105
Tensile strength, lb/sq in.	540	285	270	270	235
Elongation, %	500	720	725	820	820
Tear strength, lb/in.	44	51	58	70	40

TABLE 8

PROPERTIES OF PENTAMETHYLENE DICHLORIDE/FORMAL COPOLYMERS

Polymer No.	A19437R4	A11432-S1 A11432-S2	A19444R1	A55253
	Formal Control			
Pentamethylene dichloride, mole %	--	60	60	60
Formal, mole %	98	36	38	38
Trichloropropane, mole %	2	4	2	2
Rank	2.25	2.25	2.25	2.25
Cake Hardness	49	49	50	43
Brookfield viscosity, poises	1400	125	200	745
Compounding recipe	Stand.	Stand.[a]	Stand.	Stand.[b]
Vulcanizate Properties (Cured 24 hr. @ 77°F)[c]				
Compound No.	25961-4 d/e	25976-3	25977-4 d/e	34367-1 d/e
Shore hardness	47/53	53	48/67	44/50
100% Modulus, lb/sq in.	125/160	190	150/190	150/160
300% Modulus, lb/sq in.	325/--	--	275/--	--
Tensile strength, lb/sq in.	540/360	475	425/190	300/300
Elongation, %	500/250	280	500/100	250/215
Tear strength, lb/in.	44/53	34	54/34	40/--
Compression set, %				
At 1 hour				
158°F	71	--	97	--
-40°F	22	--	32	30
Torsional test				
Relative modulus				
T_5, -°F	40	68	70	65
T_{10}	52	72	73	69
T_{50}	63	80	80	76
T_{100}	65	84	82	79
Absolute modulus				
G_{rt} lb/sq in.	110	211	179	157
$G_{5,000}$, -°F	62	76	79	76
$G_{10,000}$	66	79	82	78
$G_{20,000}$	67	84	84	80
Tension-retraction				
TR 10, -°F	64	75	79	--
TR 30	58	71	72	--
TR 50	53	64	60	--
TR 70	42	48	35	--
TR 10-TR 70	22	27	44	--

(Table continued and footnotes on next page.)

TABLE 8 (Contd.)

Compound No.		25961-4	25976-3	25977-4	34367-1
		Formal Control			
Swelling volume, %					
SR-6	1 Day	14	30	31	--
	1 Month	-2	11	5	--
SR-10	1 Day	0	11	11	--
	1 Month	-4	19	12	--
JP-3A	1 Day	4[f]	6	6	--
	1 Month	8[f]	22[f]	7[f]	--
Adhesion, lb/in.					
After 24-hr. cure		j	g	35[i]	--
After 48-hr. in SR-6		j	h	35[i]	--
Changes after aging for 216 hr. @ 212°F					
Weight/volume loss, %		--	--	k	1.5/2
Increase in hardness		--	--	k	2

a Standard evaluation formulation with 10 instead of 7.5 parts of lead peroxide.
b Standard evaluation formulation with 0.25 part of sulfur and 1 part of maleic anhydride.
c Except where indicated otherwise, the specimens were unaged.
d Unaged.
e Aged for 72 hours at 212°F.
f Surface of specimen attacked.
g Even after adding 1 part of maleic anhydride per 100 parts of copolymer, the adhesion was poor.
h Good adhesion.
i One part of furoic acid and 0.5 part of Bakelite resin BRR18794 per 100 parts of copolymer were added.
j Poor adhesion.
k Sample shrank and case hardened; cracked when flexed after 72 hours.

TABLE 9

LOW TEMPERATURE STRESS-STRAIN DATA
FOR PENTAMETHYLENE DICHLORIDE/FORMAL COPOLYMER

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A19444R1
	Formal Control	
Formal, mole %	98	38
Trichloropropane, mole %	2	2
Pentamethylene dichloride, mole %	--	60
Rank	2.25	2.25
Cake hardness	49	50
Brookfield viscosity, poises	1400	200

Vulcanizate Properties (Cured 24 hr. @ 77°F)

Compound No.	25961-4			25977-4		
Temperature, °F	T.S.[a] lb/sq in.	Elong.[b] %	M_{SF}[c] lb/sq in.	T.S.[a] lb/sq in.	Elong.[b] %	M_{SF}[c] lb/sq in.
80	380	760	50	320	760	43
0	700	600	117	925	980	95
-30	520	380	137	730	440	166
-50	600	220	273	885	400	221
-60	1160	120	966	965	350	276
-70	1980	60	3300	1450	280	517
-80	--	--	--	1840	80	2300

a Tensile strength.
b Elongation at break.
c Modulus of Stretch at Failure, $\frac{\text{T.S.} \times 100}{\% \text{ Elong.}} = M_{SF}$.

TABLE 10

PROPERTIES OF HEXAMETHYLENE DICHLORIDE/FORMAL COPOLYMER

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A27862R1
	Formal Control	
Hexamethylene dichloride, mole %	--	54.5
Formal, mole %	98	43.5
Trichloropropane, mole %	2	2
Rank	2.25	2.25
Cake hardness	49	50
Brookfield viscosity, poises	1400	320
Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]		
Compound No.	25961-4 b/c	25981-2 b/c
Shore hardness	47/53	53/56
100% Modulus, lb/sq in.	125/160	175/175
300% Modulus, lb/sq in.	325/--	275/290
Tensile strength, lb/sq in.	540/360	575/850
Elongation, %	500/250	825/880
Tear strength, lb/in.	44/53	105/120
Compression set, %		
At 1 hour		
158°F	71	--
-40°F	22	--
Torsional test		
Relative modulus		
T_5, -°F	40/52	56/63
T_{10}	52/57	61/65
T_{50}	63/65	74/75
T_{100}	65/66	83/86
Absolute modulus		
G_{rt}, lb/sq in.	119/221	185/197
$G_{5,000}$, -°F	62/62	70/69
$G_{10,000}$	66/65	77/76
$G_{20,000}$	67/68	86/86

(Table continued and footnotes on next page.)

TABLE 10 (Contd.)

Compound No.		25961-4	25981-2
		Formal Control	
Tension-retraction			
TR10, -°F		64	88
TR30		58	80
TR50		53	55
TR70		42	Did not reach
TR10-TR70		22	--
Swelling volume, %			
SR-6	1 Day	14	11
	2 Weeks	-2	8[e]
SR-10	1 Day	0	6
	2 Weeks	-2	6
JP-3A	1 Day	4[d]	21[d]
	2 Weeks	8[d]	30[d]
Adhesion, lb/in.			
After 24-hr. cure		Poor	e
After 48-hr. in SR-6		Poor	Poor

a Except where indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Surface of specimen attacked.
e Poor adhesion without additives. When 0.25 part each of maleic anhydride and furoic acid were added to the formulation, the adhesion was somewhat improved.

TABLE 11

PROPERTIES OF ETHYLENE DICHLORIDE/FORMAL COPOLYMERS
(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A19450R1	A19450R2	A19450R5
	Formal Control			
Formal, mole %	98	88	78	68
Trichloropropane, mole %	2	2	2	2
Ethylene dichloride, mole %	--	10	20	30
Rank	2.25	2.25	2.25	2.25
Cake hardness	49	47	49	50
Brookfield viscosity, poises	1400	1700	1700	2420
	Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]			
Compound No.	25961-4 b/c	25971-4 b/c	25971-5 b/c	25971-6 b/c
Shore hardness	47/53	48/52	47/50	49/50
100% Modulus, lb/sq in.	125/160	140/190	110/160	100/175
300% Modulus, lb/sq in.	340/300	--/--	--/--	--/--
Tensile strength, lb/sq in.	540/360	320/290	340/300	230/360
Elongation, %	500/250	270/190	280/260	275/260
Compression set, %				
At 1 hour				
180°F	72	53	57	77
158°F	71	59	77	63
-20°F	18	15	54	18
-40°F	22	64	71	56
Torsional test				
Relative modulus				
T_5, -°F	40/52	50/47	47/43	41/41
T_{10}	52/57	52/52	50/49	44/47
T_{50}	63/65	60/60	58/56	56/54
T_{100}	65/66	62/62	61/59	60/57

(Table continued and footnotes on next page.)

TABLE 11 (Contd.)

Compound No.	25961-4	25971-4	25971-5	25971-6
	Formal Control			
Ethylene dichloride, mole %	--	10	20	30
	b/c	b/c	b/c	b/c
Torsional test				
Absolute modulus				
G_{rt}, lb/sq in.	119/221	170/150	162/132	--/221
$G_{5,000}$, -°F	62/60	60/58	57/55	56/53
$G_{10,000}$	66/65	63/61	60/58	59/56
$G_{20,000}$	67/68	65/64	62/61	61/59
Tension-retraction				
TR10, -°F	64	--	59	56
TR30	58	--	52	49
TR50	53	--	46	43
TR70	42	--	34	31
TR10-TR70	22	--	25	25
Swelling volume, %				
SR-6 1 Day	14	13	15	13
1 Month	-2	7	5	7
SR-10 1 Day	0	5	5	3
1 Month	-4	11	8	7
JP-3A 1 Day	4[d]	3	0	3
1 Month	8[d]	6[d]	5[d]	5[d]
Adhesion,				
After 24-hr. cure	--	Poor	--	Poor
After 48-hr. immersion in SR-6	--	Poor	--	Poor

a Except where indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Surface of specimen attacked.

TABLE 12

LOW TEMPERATURE STRESS-STRAIN DATA FOR ETHYLENE DICHLORIDE/FORMAL COPOLYMERS

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A19450R1	A19450R2	A19450R3
	Formal Control			
Formal, mole %	98	88	78	68
Trichloropropane, mole %	2	2	2	2
Ethylene dichloride, mole %	-	10	20	30
Rank	2.25	2.25	2.25	2.25
Cake hardness	49	47	49	50
Brookfield viscosity, poises	1400	1790	1700	2420

Vulcanizate Properties (Cured 24 hr. @ 77°F)

Compound No.	------25961-4------			------25971-4------			------25971-5------			------25971-6------		
Temperature, °F	T.S.[a] lb/sq in.	Elong.[b] %	M_{SF}[c] lb/sq in.	T.S.[a] lb/sq in.	Elong.[b] %	M_{SF}[c] lb/sq in.	T.S.[a] lb/sq in.	Elong.[b] %	M_{SF}[c] lb/sq in.	T.S.[a] lb/sq in.	Elong.[b] %	M_{SF}[c] lb/sq in.
80	380	760	50	300	480	62	290	360	81	260	470	55
-30	520	380	137	480	370	130	390	350	112	640	380	168
-50	600	220	273	840	390	216	600	340	176	1100	330	333
-60	1160	120	966	1080	230	469	1230	120	1025	1360	160	850
-70	1980	60	3300	2400	60	4000	2800	40	7000	2200	90	2444

a Tensile strength.

b Elongation at break.

c Modulus of stretch at failure, $\frac{\text{T.S.} \times 100}{\% \text{ Elong.}} = M_{SF}$

TABLE 13

PROPERTIES OF DIBROMOSUCCINIC ACID/FORMAL COPOLYMERS

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A27851R	A27851R2	A27851R3
	Formal			
α,α'-Dibromosuccinic acid, mole %	Control	10	20	30
Formal, mole %	98	88	78	68
Trichloropropane, mole %	2	2	2	2
Rank	2.25	2.25	2.25	2.25
Cake hardness	49	47	49	51
Brookfield viscosity, poises	1400	335	505	190
Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]				
Compound No.	25961-4 b/c	28114-1 b/c	28114-2 b/c	28114-3 b/c
Shore hardness	47/53	53/53	53/57	53/56
100% Modulus, lb/sq in.	125/160	225/260	200/250	200/260
300% Modulus, lb/sq in.	325/--	450/--	475/--	475/--
Tensile strength, lb/sq in.	540/360	750/260	560/300	610/275
Elongation, %	500/250	490/100	340/140	360/120
Compression set, %				
At 1 hour				
180°F	72	101	97	98
158°F	71	97	92	97
-20°F	18	15	19	38
-40°F	22	32	22	17
Torsional test				
Relative modulus				
T_5, -°F	40/52	54/57	56/56	56/55
T_{10}	52/57	57/59	58/59	58/58
T_{50}	63/65	65/66	65/67	66/66
T_{100}	65/66	70/72	70/72	71/71
Absolute modulus				
G_{rt}, lb/sq in.	119/221	233/246	250/330	282/338
$G_{5,000}$, -°F	62/62	61/63	60/61	60/61
$G_{10,000}$	66/65	64/66	64/65	63/65
$G_{20,000}$	67/68	68/70	69/69	69/69
Tension-retraction				
TR10, -°F	64	58	65	58
TR30	58	56	64	56
TR50	53	55	60	53
TR70	42	47	52	43
TR10-TR70	22	11	13	15

(Table continued and footnotes on next page.)

TABLE 13 (Contd.)

Compound No.		25961-4	28114-1	28114-2	28114-3
α,α'-Dibromosuccinic acid, mole %		Formal Control	10	20	30
Swelling volume, %					
SR-6	1 Day	14	10	12	12
	1 Month	-2	-7	-1	-4
SR-10	1 Day	0	-3	0	0
	1 Month	-4	-8	-3	-6
JP-3A	1 Day	4[c]	1	1	2
	1 Month	8[d]	3[d]	5[d]	5[d]
Adhesion					
After 24-hr. cure		Poor	--	Poor	Poor
After 48-hr. immersion in SR-6		Poor	--	Poor	Poor

a Unless indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Surface of specimen attacked.

TABLE 14

PROPERTIES OF GLYCEROL-a, B-DICHLOROHYDRIN/FORMAL COPOLYMERS

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A19447R2	A19447R3	A19447R4	A27858R3	A27858R4
Glycerol- α,β-dichlorohydrin, mole %	Formal Control	9.1[a]	18.2[a]	27.3[a]	20	30
Formal, mole %	98	88.9	79.8	20.7	78	68
Trichloropropane, mole %	2	2	2	2	2	2
Rank	2.25	2.25	2.25	2.25	2.25	2.25
Cake hardness	49	49	49	53	50	52
Brookfield viscosity, poises	1400	730	1220	1640	145	160
	Vulcanizate Properties (Cured 24 hr. @ 77°F)[b]					
Compound No.	25961-4 d/e	25972-2 d/e	25972-3 d/e	25972-4 d/e	25978-2[c] d/e	25978-3[c] d/e
Shore hardness	47/53	53/56	54/57	57/60	53/63	60/63
100% Modulus, lb/sq in.	125/160	200/--	220/--	160/--	210/375	--
300% Modulus, lb/sq in.	325/--	--	--	--	--	--
Tensile strength, lb/sq in.	540/360	360/240	325/200	160/240	300/400	250/290
Elongation, %	500/250	220/100	180/70	100/60	290/110	70/60
Tear strength, lb/in.	44/53	31/36	--/27	--	35/26	19/--
Compression set, %						
At 1 hour						
180°F	72	97	98	95	--	--
158°F	71	94	96	67	--	--
-20°F	18	14	24	10	--	--
-40°F	22	21	31	18	--	--
Torsional test						
Relative modulus						
T_5, -°F	40/52	55/52	53/51	50/49	51/51	49/46
T_{10}	52/57	60/60	58/58	53/56	54/56	52/52
T_{50}	63/65	65/67	66/67	62/65	61/63	59/60
T_{100}	65/66	67/69	67/69	66/68	62/64	61/63

(Table continued on next page.)

TABLE 14 (Contd.)

Compound No.	25961-4	25972-2	25972-3	25972-4	25978-2	25978-3
Glycerol-α, β-dichlorohydrin, mole %	Formal Control d/e	9.1[a] d/e	18.2[a] d/e	27.3[a] d/e	20 d/e	30 d/e
Torsional test						
Absolute modulus						
G_{rt}, lb/sq in.	119/221	218/285	238/378	180/348	202/296	275/535
$G_{5,000}$, $-^{o}F$	62/62	62/63	62/60	60/59	58/59	55/53
$G_{10,000}$	66/65	65/66	65/65	64/64	61/62	57/55
$G_{20,000}$	67/68	67/68	67/68	68/67	63/63	60/58
Tension-retraction, %						
TR10, $-^{o}F$	64	63	f	f	f	f
TR30	58	59	f	f	f	f
TR50	53	55	f	f	f	f
TR70	42	47	f	f	f	f
TR10-TR70	22	16	f	f	f	f
Swelling volume, %						
SR-6 1 Day	14	11	13	12	2	0
1 Month	-2	2	2	8	-3	0
1 Day	0	0	1	0	0	2
1 Month	-4	-3	-4	-3	-4	0
1 Day	4[g]	2	0	0	3	2
2 Weeks	8[g]	4[g]	3[g]	5[g]	4[g]	4[g]
Adhesion, lb/sq in.						
After 24-hr. cure	Poor	Poor	Poor	Poor	7[h]	--
After 48-hr. in SR-6	Poor	Poor	Poor	Poor	7[h]	--

(Footnotes on next page.)

TABLE 14 (Contd.)

Footnotes:

a Composition after redistribution with 10%, by weight, of ZL-109.
b Unless indicated otherwise, the specimens were unaged.
c Instead of 7.5 parts of lead peroxide, 10 parts were used.
d Unaged.
e Aged for 72 hours at 212°F.
f The TR specimens broke at 100% elongation.
g Surface of specimen attacked.
h The addition of 0.25 part each of maleic anhydride and furoic acid improved the adhesion which was poor initially.

TABLE 15

PROPERTIES OF DICHLORODIETHYL ETHER/FORMAL COPOLYMERS

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A27866R1	A27866R2	A27866R3
	Formal			
Dichlorodiethyl ether, mole %	Control	10	20	30
Formal, mole %	98	88	78	68
Trichloropropane, mole %	2	2	2	2
Rank	2.25	2.25	2.25	2.25
Cake hardness	49	49	52	54
Brookfield viscosity, poises	1400	200	290	170
Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]				
Compound No.	25961-4 b/c	25977-1 b/c	25977-2 b/c	25977-3 b/c
Shore hardness	47/53	53/67	46/58	53/63
100% Modulus, lb/sq in.	125/160	225/--	160/--	190/--
300% Modulus, lb/sq in.	325/--	--	--	--
Tensile strength, lb. sq in.	540/360	360/150	300/160	375/210
Elongation, %	500/250	240/50	340/45	250/25
Tear strength, lb/in.	44/53	39/28	32/27	30/23
Compression set, %				
At 1 hour				
158°F	71	100	99	97
-40°F	22	26	35	18
Torsional test				
Relative modulus				
T_5, -°F	40/52	56	52	58
T_{10}	52/57	61	60	62
T_{50}	63/65	66	65	67
T_{100}	65/66	68	67	69
Absolute modulus				
G_{rt}, lb/sq in.	119/221	187	136	250
$G_{5,000}$, -°F	62/62	64	64	64
$G_{10,000}$	66/65	66	67	66
$G_{20,000}$	67/68	69	70	68
Tension-retraction, %				
TR10, -°F	64	64	62	61
TR30	58	60	55	59
TR50	53	55	45	53
TR70	42	45	32	43
TR10-TR70	22	19	30	18

(Table continued and footnotes on next page.)

TABLE 15 (Contd.)

Compound No.		25961-4	25977-1	25977-2	25977-3
Dichlorodiethyl ether, mole %		Formal Control	10	20	30
Swelling volume, %					
SR-6	1 Day	14	9	9	5
	1 Month	-2	-13	-5	-12
SR-10	1 Day	0	5	2	0
	1 Month	-4	-10	-4	-21
JP-3A	1 Day	4[d]	0	0	1
	1 Month	8[d]	4[d]	0[d]	-2[d]
Adhesion, lb/in.					
After 24-hr. cure		Poor	e	15[e]	18[e]
After 48-hr. in SR-6		Poor	e	30[e]	24[e]

a Unless indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Surface of specimen attacked.
e The addition of 1 part of furoic acid and 0.5 part of BRR-18794 improved the adhesion which was poor initially.

TABLE 16

PROPERTIES OF O-XYLYLENE DICHLORIDE/FORMAL COPOLYMERS

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A27872R1	A27872R2
	Formal		
o-Xylylene dichloride, mole %	Control	10	20
Formal, mole %	98	88	78
Trichloropropane, mole %	2	2	2
Rank	2.25	2.25	2.25
Cake hardness	49	44	40
Brookfield viscosity, poises	1400	880	2520
Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]			
Compound No.	25961-4	25982-2	25986-1
	b/c	b/c	b/c
Shore hardness	47/53	49/52	46/43
100% Modulus, lb/sq in.	125/160	160/110	150/150
300% Modulus, lb/sq in.	325/--	310/360	225/240
Tensile strength, lb/sq in.	540/360	550/440	360/420
Elongation, %	500/250	520/375	670/560
Tear strength, lb/in.	44/53	64/65	65/66
Compression set, %			
At 1 hour			
158°F	71	97	80
-40°F	22	39	22
Torsional test			
Relative modulus			
T_5, -°F	40/52	32/26	2/11
T_{10}	52/57	38/33	6/20
T_{50}	63/65	47/42	22/25
T_{100}	65/66	50/44	45/30
Absolute modulus			
G_{rt}, lb/sq in.	119/221	156/176	90/107
$G_{5,000}$, -°F	62/62	44/39	24/24
$G_{10,000}$	66/65	47/42	28/29
$G_{20,000}$	67/68	51/45	31/31
Tension-retraction			
TR10, -°F	64	47	22
TR30	58	42	13
TR50	53	35	4
TR70	42	24	+11
TR10-TR70	22	23	11

(Table continued and footnotes on next page.)

TABLE 16 (Contd.)

Compound No.		25961-4	25982-2	25986-1
O-Xylylene dichloride, mole %		Formal Control	10	20
Swelling volume, %				
SR-6	1 Day	14	3	0
	1 Month	-2	0	0
SR-10	1 Day	0	2	0
	1 Month	-4	0	0
JP-3A	1 Day	4[d]	4[d]	1[d]
	2 Weeks	8[d]	8[d]	2[d]
Adhesion, lb/in.				
After 24-hr. cure		Poor	e	--
After 48-hr. in SR-6		Poor	Poor	--

a Unless indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Surface of specimen attacked.
e The addition of 0.25 part each of maleic anhydride and furoic acid improved the adhesion which was initially poor.

TABLE 17

PROPERTIES OF N-METHYL DICHLORODIETHYLAMINE/FORMAL COPOLYMERS
(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A29457A1-1	A29457A1-2
	Formal		
N-Methyl dichlorodiethylamine, mole %	Control	10	20
Formal, mole %	98	88	78
Trichloropropane, mole %	2	2	2
Rank	2.25	2.25	2.25
Cake hardness	49	45	44
Brookfield viscosity, poises	1400	370	635
Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]			
Compound No.	25961-4 b/c	25986-2 b/c	25986-3 b/c
Shore hardness	47/53	50/53	56/63
100% Modulus, lb/sq in.	125/160	175/175	200/350
300% Modulus, lb/sq in.	325/--	325/375	575/--
Tensile strength, lb/sq in.	540/360	650/475	625/575
Elongation, %	500/250	700/390	390/260
Tear strength, lb/in.	44/53	82/66	141/145
Compression set, %			
At 1 hour			
158°F	71	81	--
-40°F	22	22	--
Torsional test			
Relative modulus			
T_5, -°F	40/52	52/48	54/49
T_{10}	52/57	56/54	58/54
T_{50}	63/65	63/61	64/61
T_{100}	65/66	66/63	66/64
Absolute modulus			
G_{rt}, lb/sq in.	119/221	135/225	195/342
$G_{5,000}$, -°F	62/62	62/57	63/58
$G_{10,000}$	66/65	65/60	66/60
$G_{20,000}$	67/68	68/63	69/63
Tension-retraction			
TR10, -°F	64	61	63
TR30	58	56	56
TR50	53	45	48
TR70	42	30	37
TR10-TR70	22	31	26

(Table continued and footnotes on next page.)

TABLE 17 (Contd.)

Compound No.		25961-4	25986-2	25986-3
N-Methyl dichlorodiethylamine, mole %		Formal Control	10	20
Swelling volume, %				
SR-6	1 Day	14	3	3
	1 Month	-2	0	0
SR-10	1 Day	0	2	2
	1 Month	-4	0	-2
JP-3A	1 Day	4[d]	4[d]	4
	2 Weeks	8[d]	6[d]	5[d]
Adhesion, lb/in.				
After 24-hr. cure		Poor	--	e
After 48-hr. in SR-6		Poor	--	e

a Unless indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Surface of specimen attacked.
e The addition of 0.25 part each of maleic anhydride and furoic acid yielded excellent adhesion which was initially poor.

TABLE 18

PROPERTIES OF BIS(2-CHLOROETHYL) AMINE/FORMAL COPOLYMERS

Polymer No.	A19437R4	A29555H1	A29555H2
	Formal Control		
Bis(2-Chloroethyl)amine, mole %	--	10	20
Formal, mole %	98	88	78
TCP, mole %	2	2	2
Rank	2.25	2.25	2.25
Cake hardness	49	41	40
Brookfield viscosity, poises	1400	55	65
Compounding recipe	Stand.	a	a
Vulcanizate Properties (Cured 24 hr. @ 77°F)[b]			
Compound No.	25961-4 c/d	25998-1 c/d	25998-2 c/d
Shore hardness	47/53	53/60	48/60
100% Modulus, lb/sq in.	125/160	200/235	175/235
300% Modulus, lb/sq in.	325/--	390/475	340/485
Tensile strength, lb/sq in.	540/360	525/535	425/525
Elongation, %	500/250	465/360	430/360
Tear strength, lb/ in.	44/53	53/72	44/60
Compression set, %			
At 1 hour			
158°F	71	112	100
-40°F	22	14	22
Torsional test			
Relative modulus			
T_5, -°F	40/52	45/49	45/49
T_{10}	52/57	54/54	53/55
T_{50}	63/65	60/62	61/62
T_{100}	65/66	63/65	63/65
Absolute modulus			
G_{rt}, lb/sq in.	119/221	158/267	137/251
$G_{5,000}$, -°F	62/62	59/58	60/59
$G_{10,000}$	66/65	61/61	62/63
$G_{20,000}$	67/68	65/65	65/64

(Table continued and footnotes on next page.)

TABLE 18 (Contd.)

Compound No.		25961-4	25998-1	25998-2
Bis(2-chloroethyl)amine, mole %		Formal Control	10	20
		c/d	c/d	c/d
Tension-retraction test				
TR10, -°F		64	61	60
TR30		58	55	53
TR50		53	46	42
TR70		42	33	28
TR10-TR70		22	28	32
Decrease in weight/volume After 72-hr. aging, %		18/16[e]	24/20[e]	24/21[e]
Swelling volume, %				
SR-6	1 Day	14	13	14
	1 Month	-2	3	7
SR-10	1 Day	0	1	1
	1 Month	-4	-2	0
JP-3A	1 Day	4[f]	6[f]	3[f]
	1 Month	8[f]	6[f]	5[f]
Adhesion				
After 24-hr. cure		Poor	None	Poor
After 24-hr. cure[g]		Excellent	Good	--
After 48-hr. in SR-6		Poor	None	Poor
After 48-hr. in SR-6[g]		Excellent	Good	--

a Standard formulation except that 2.8 parts of lead stearate, 15 parts lead peroxide and 0.25 part of sulfur were used.
b Unless indicated otherwise, the specimens were unaged.
c Unaged.
d Aged 72 hours at 212°F.
e Specimens did not crack when flexed 180°F.
f Surface of specimen attacked.
g Adhesion additive consisting of 0.25 part of maleic anhydride and 0.25 part of furoic acid included in the formulation.

TABLE 19

PROPERTIES OF DICHLOROPROPIONITRILE/FORMAL COPOLYMERS

Polymer No.	A19437R4	A29534W1	A29534W2
	Formal Control		
Dichloropropionitrile, mole %	--	10	20
Formal, mole %	98	88	78
Trichloropropane, mole %	2	2	2
Rank	2.25	2.25	2.25
Cake hardness	49	40	37
Brookfield viscosity, poises	1400	245	350
Compounding recipe	Stand.	a	a
Vulcanizate Properties (Cured 24 hr. @ 77°F)[b]			
Compound No.	25961-4 c/d	34378-1 c/c	34382-1 c/d
Shore hardness	47/53	53/53	47/53
100% Modulus, lb/sq in.	125/160	160/160	125/175
300% Modulus, lb/sq in.	325/--	--	--
Tensile strength, lb/sq in.	540/360	325/250	260/310
Elongation, %	500/250	270/160	210/210
Tear strength, lb/in.	44/53	30/35	21/39
Compression set, %			
At 1 hr.			
158°F	71	25	45
-40°F	22	26	30
Torsional test			
Relative modulus			
T_5, -°F	40/52	54/50	48/43
T_{10}	52/57	57/56	52/49
T_{50}	63/65	62/61	61/58
T_{100}	65/66	64/62	64/59
Absolute modulus			
G_{rt}, lb/sq in.	119/221	245/182	141/117
$G_{5,000}$, -°F	62/62	60/61	60/56
$G_{10,000}$	66/65	62/63	63/60
$G_{20,000}$	67/68	66/64	69/62

(Table continued and footnotes on next page.)

TABLE 19 (Contd.)

Compound No.		25961-4	34378-1	34382-1
Tension-retraction test				
TR 10, -°F		64	61	60
TR 30		58	56	54
TR 50		53	50	45
TR 70		42	40	35
TR 10-TR 70		22	21	25
Decrease in weight/volume				
After 72-hr. aging, %		18/16	4/4	10/9
Swelling volume, %				
SR-6	1 Day	14	13	13
	1 Month	-2	16	13
SR-10	1 Day	0	1	1
	1 Month	-4	3	2
JP-3A	1 Day	4[e]	2	4
	1 Month	8[e]	5[e]	8
Adhesion				
After 24 hr. cure		Poor	Poor	Poor
After 48 hr. in SR-6		Poor	Poor	Poor

a Standard formulation except that 2.8 parts of lead stearate and 15 parts of lead peroxide were used.
b Unless indicated otherwise, the specimens were unaged.
c Unaged.
d Aged for 72 hours at 212°F.
e Surface of specimen attacked.

TABLE 20

PROPERTIES OF HEXAMETHYLENE DICHLORIDE/TRIGLYCOL DICHLORIDE/ FORMAL TERPOLYMERS

(Compounded by Standard Evaluation Recipe, Appendix B)

Polymer No.	A19437R4	A29535W1
	Formal Control	
Hexamethylene dichloride, mole %	--	50
Triglycol dichloride, mole %	--	25
Formal, mole %	98	23
Trichloropropane, mole %	2	2
Rank	2.25	2.25
Cake hardness	49	47
Brookfield viscosity, poises	1400	365
Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]		
Compound No.	25961-4 b/c	34366-1 b/c
Shore hardness	47/53	52/53
100% Modulus, lb/sq in.	125/160	150/175
300% Modulus, lb/sq in.	325/160	150/175
Tensile strength, lb/sq in.	540/360	350/315
Elongation, %	500/250	340/280
Tear strength, lb/in.	44/53	38/38
Compression set, %		
158°F at 1 hour	71	51
-40°F at 1 hour	22	21
Torsional test		
Relative modulus		
T_5, -°F	40	71/68
T_{10}	52	74/74
T_{50}	63	80/79
T_{100}	65	82/83
Absolute modulus		
G_{rt}, lb/sq in.	119	158/159
$G_{5,000}$, -°F	62	76/77
$G_{10,000}$	66	78/80
$G_{20,000}$	67	80/84

(Table continued and footnotes on next page.)

TABLE 20 (Contd.)

Compound No.		25961-4	34366-1
		Formal Control	
Tension-retraction test			
TR10, -°F		64	77
TR30		58	74
TR50		53	68
TR70		42	50
TR10-TR70		22	27
Weight/volume loss after aging @ 212°F, %		18/16[c]	1.5/2[d]
Swelling volume, %			
SR-6	1 Day	14	46
	1 Month	-2	47
SR-10	1 Day	0	4
	1 Month	-4	9
JP-3A	1 Day	4[e]	--
	1 Month	8[e]	--

a . Unless indicated otherwise, the specimens were unaged.
b Unaged.
c Aged 72 hours at 212°F.
d Aged 216 hours at 212°F.
e Surface of specimen attacked.

TABLE 21

PROPERTIES OF HEXAMETHYLENE DICHLORIDE/PENTAMETHYLENE DICHLORIDE/FORMAL TERPOLYMER

Polymer No.	A19437R4	A55256V
	Formal Control	
Hexamethylene dichloride, mole %	--	21.2
Pentamethylene dichloride, mole %	--	21.2
Formal, mole %	98	55.6
Trichloropropane, mole %	2	2
Rank	2.25	2.25
Cake hardness	49	45
Brookfield viscosity, poises	1400	130
Compounding recipe	Stand.	a
Vulcanizate Properties (Cured 24 hr. @ 77°F)[b]		
Compound No.	25961-4 c/d	34380-1 c/d
Shore hardness	47/53	47/50
100% Modulus, lb/sq in.	125/160	140/150
300% Modulus, lb/sq in.	325/--	240/260
Tensile strength, lb/sq in.	540/360	420/390
Elongation, %	500/250	760/650
Tear strength, lb/in.	44/53	84/80
Compression set, %		
At 1 hour		
158°F	71	--
-40°F	22	--
Torsional test		
Relative modulus		
T_5, -°F	40/52	67/70
T_{10}	52/57	71/74
T_{50}	63/65	81/81
T_{100}	65/66	83/83
Absolute modulus		
G_{rt}, lb/sq in.	119/221	158/214
$G_{5,000}$	62/62	80/79
$G_{10,000}$	66/65	83/82
$G_{20,000}$	67/68	85/84

(Table continued and footnotes on next page.)

TABLE 21 (Contd.)

Compound No.		25961-4	34380-1
Tension-retraction test			
TR10, -°F		64	75
TR30		58	70
TR50		53	54
TR70		42	30
TR10-TR70		22	45
Decrease in weight/volume			
After 72 hr. aging at 212°F, %		18/16	10/9
Swelling volume, %			
SR-6	1 Day	14	31
	1 Month	-2	26
SR-10	1 Week	0	4
	1 Month	-4	2
JP-3A	1 Day	4[e]	10
	1 Month	8[e]	17[e]
Adhesion			
After 24 hr. cure		Poor	Poor
After 48 hr. in SR-6		Poor	Poor

a Test formulation in parts: terpolymer, 100; zinc sulfide (ZS-800), 50; lead stearate, 2.8; lead peroxide, 15; sulfur, 0.25.
b Unless indicated otherwise, the specimens were unaged.
c Unaged.
d Aged for 72 hours at 212°F.
e Surface of specimen attacked.

FIGURE 1

EFFECT OF POLYSULFIDE RANK ON PHYSICAL PROPERTIES OF UNAGED FORMAL POLYMERS

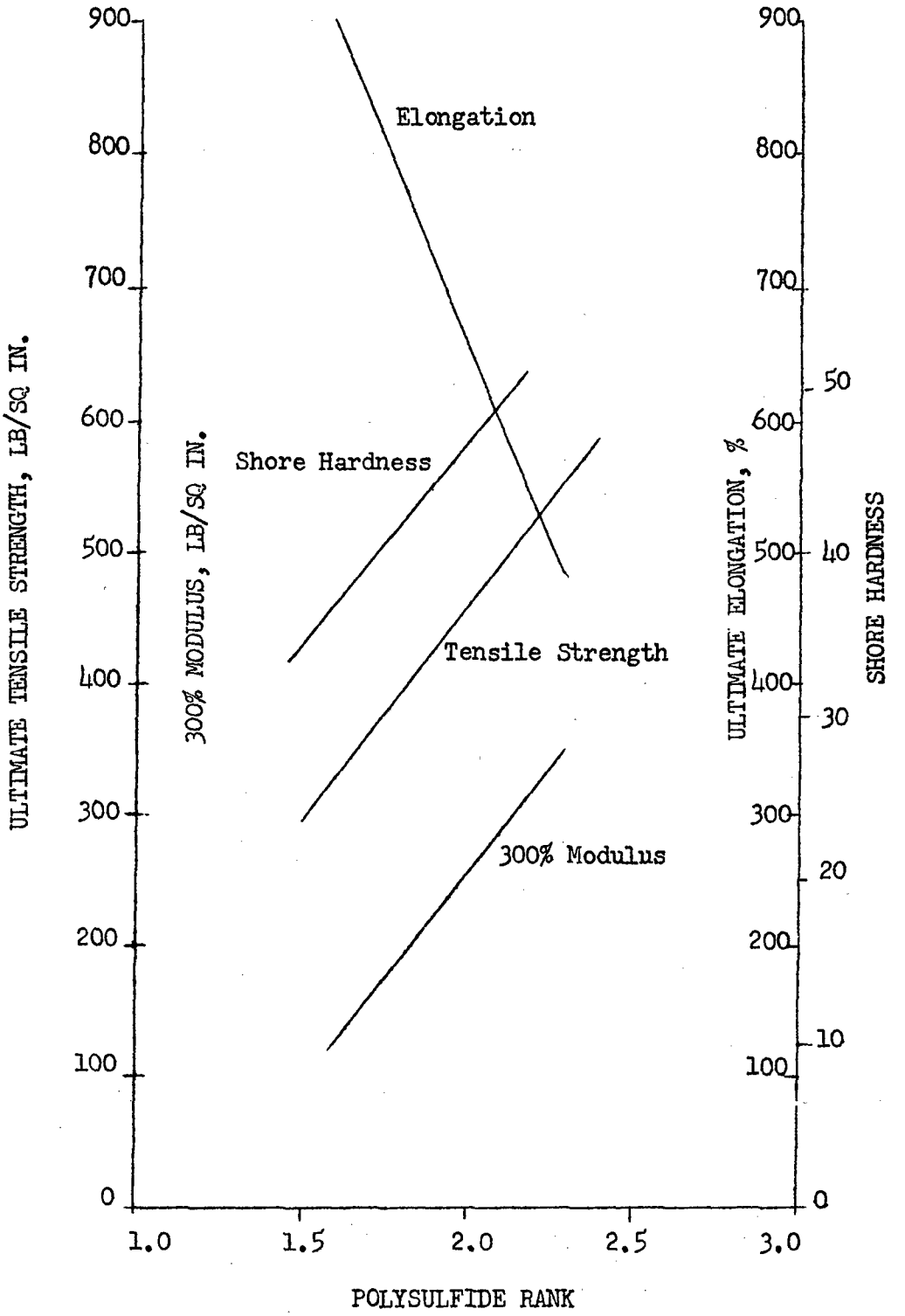


FIGURE 2

ABSOLUTE TORSIONAL MODULUS VERSUS TEMPERATURE OF PENTAMETHYLENE AND HEXAMETHYLENE COPOLYMERS

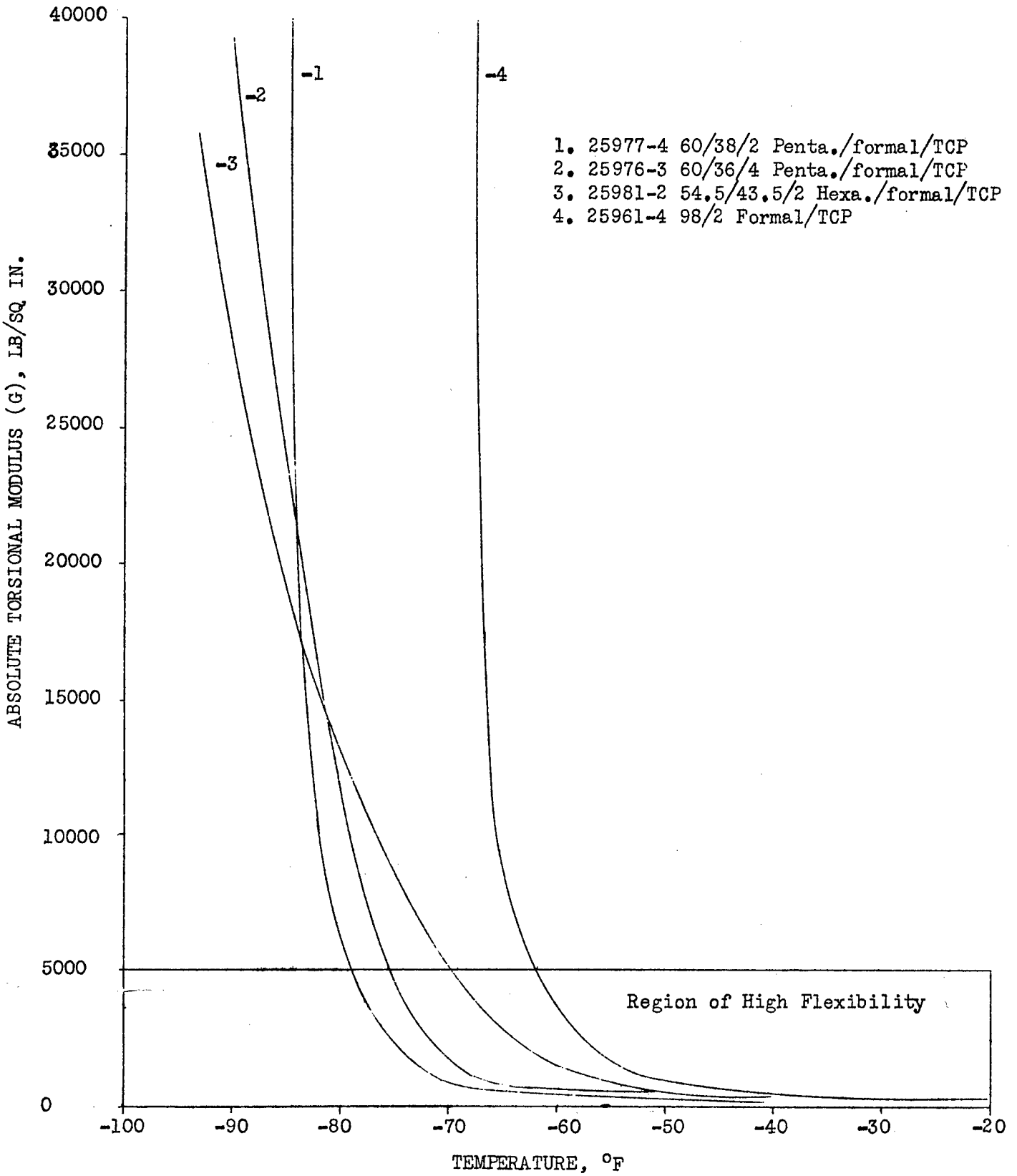


FIGURE 3

TENSION-RETRACTION VERSUS TEMPERATURE

OF PENTAMETHYLENE AND HEXAMETHYLENE COPOLYMERS

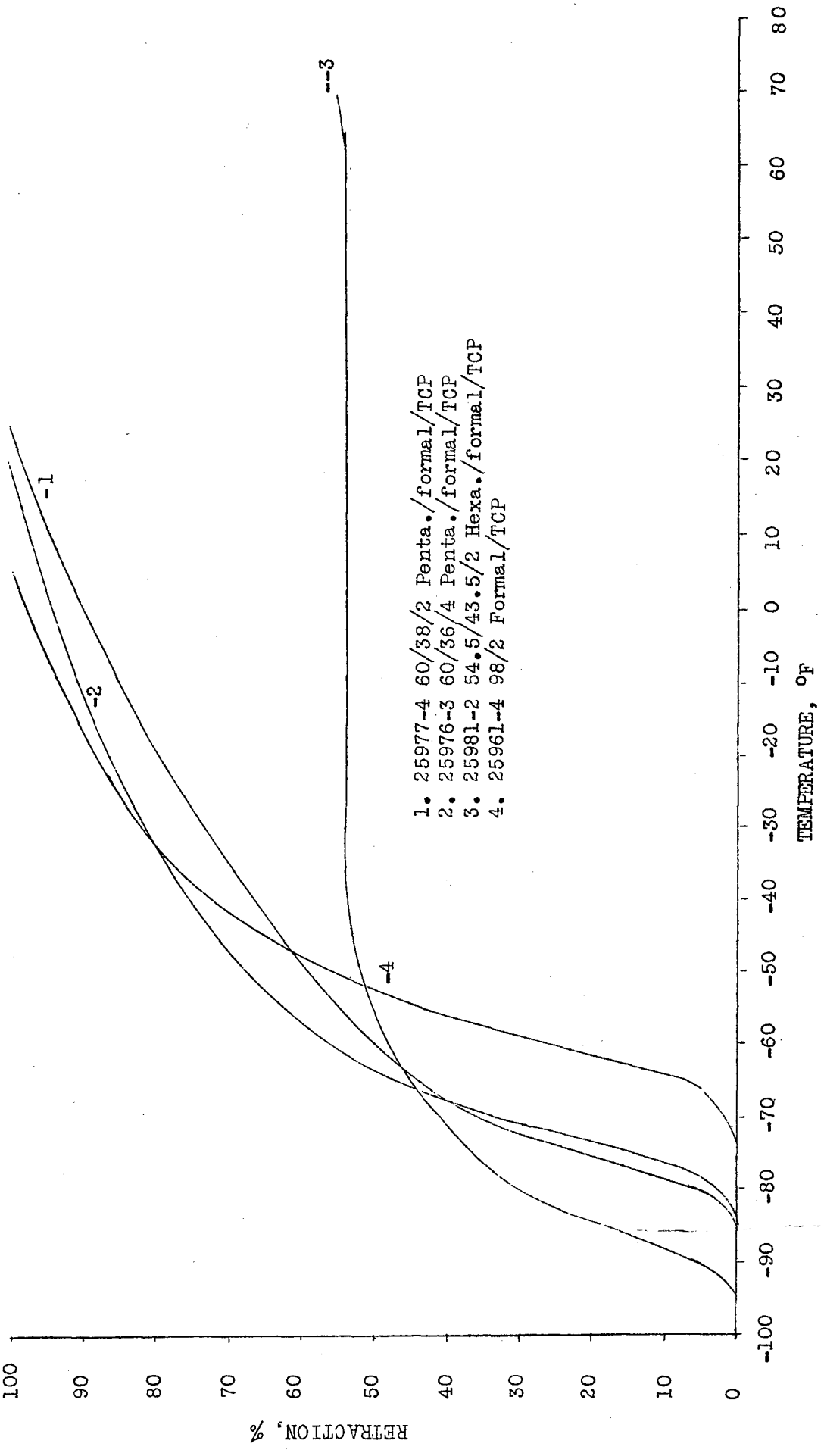


FIGURE 4

ULTIMATE TENSILE STRENGTH VERSUS TEMPERATURE
OF PENTAMETHYLENE COPOLYMERS

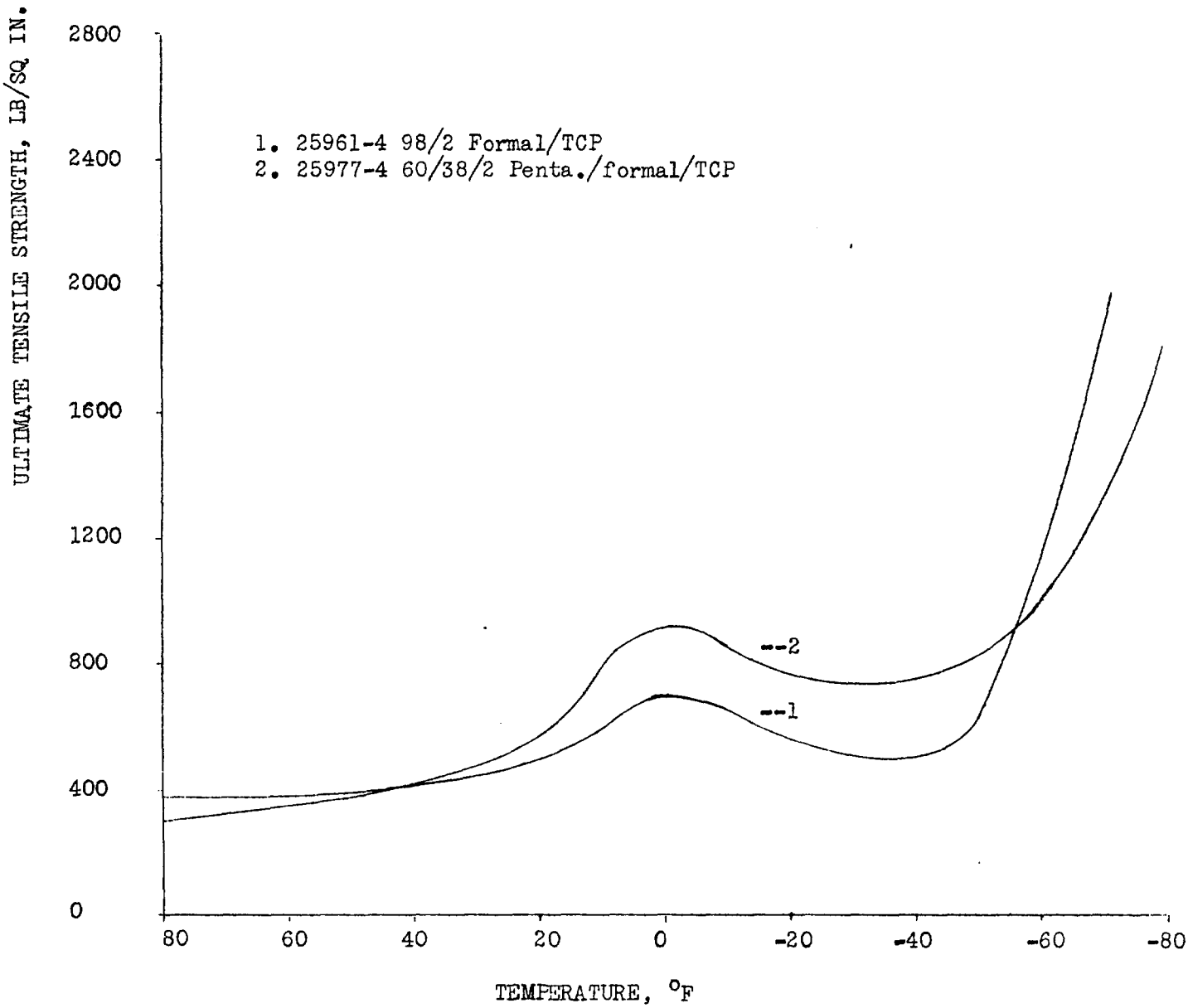


FIGURE 5

ULTIMATE ELONGATION VERSUS TEMPERATURE
OF PENTAMETHYLENE COPOLYMERS

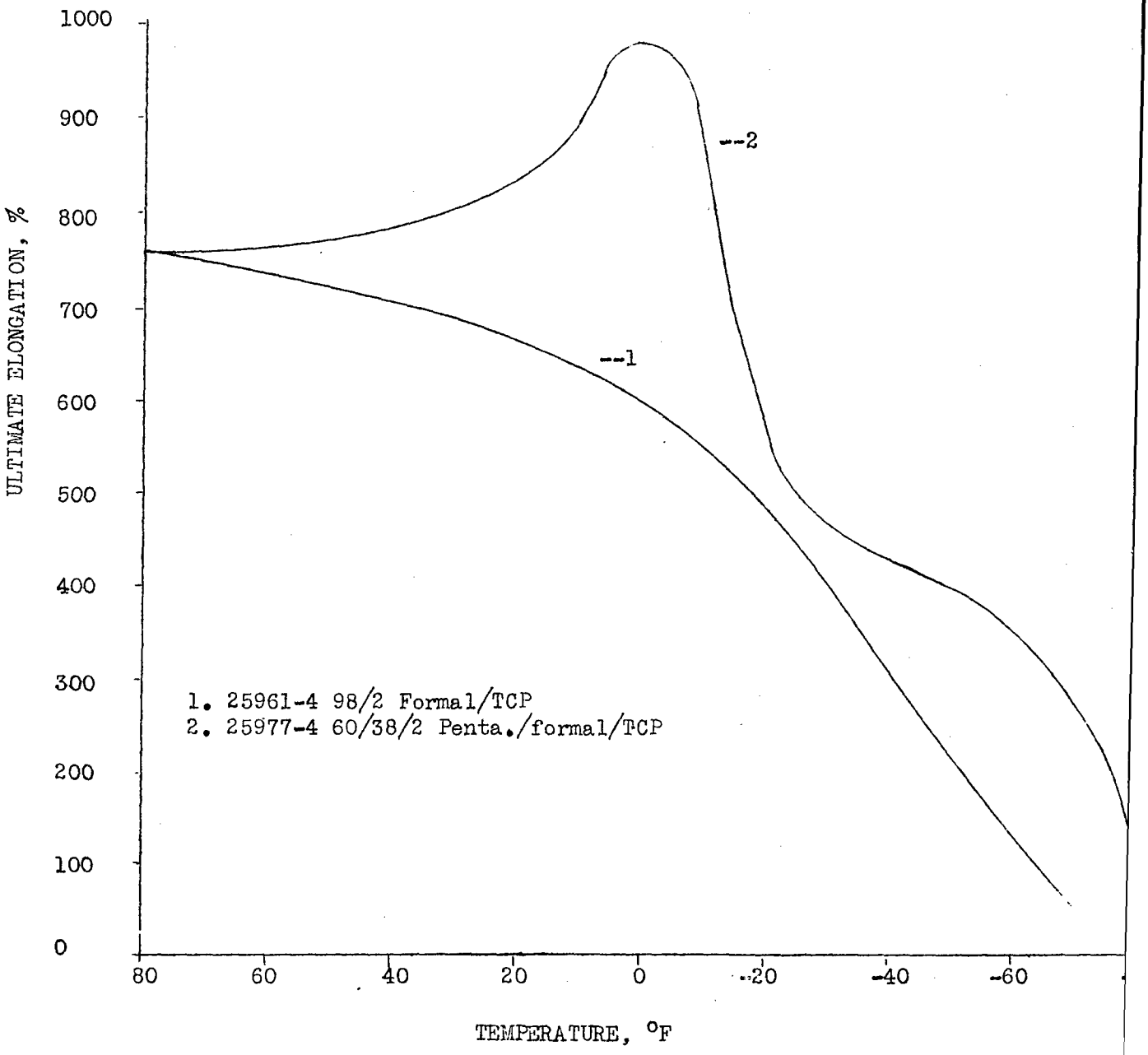


FIGURE 6

MODULUS OF STRETCH AT FAILURE VERSUS TEMPERATURE OF PENTAMETHYLENE COPOLYMERS

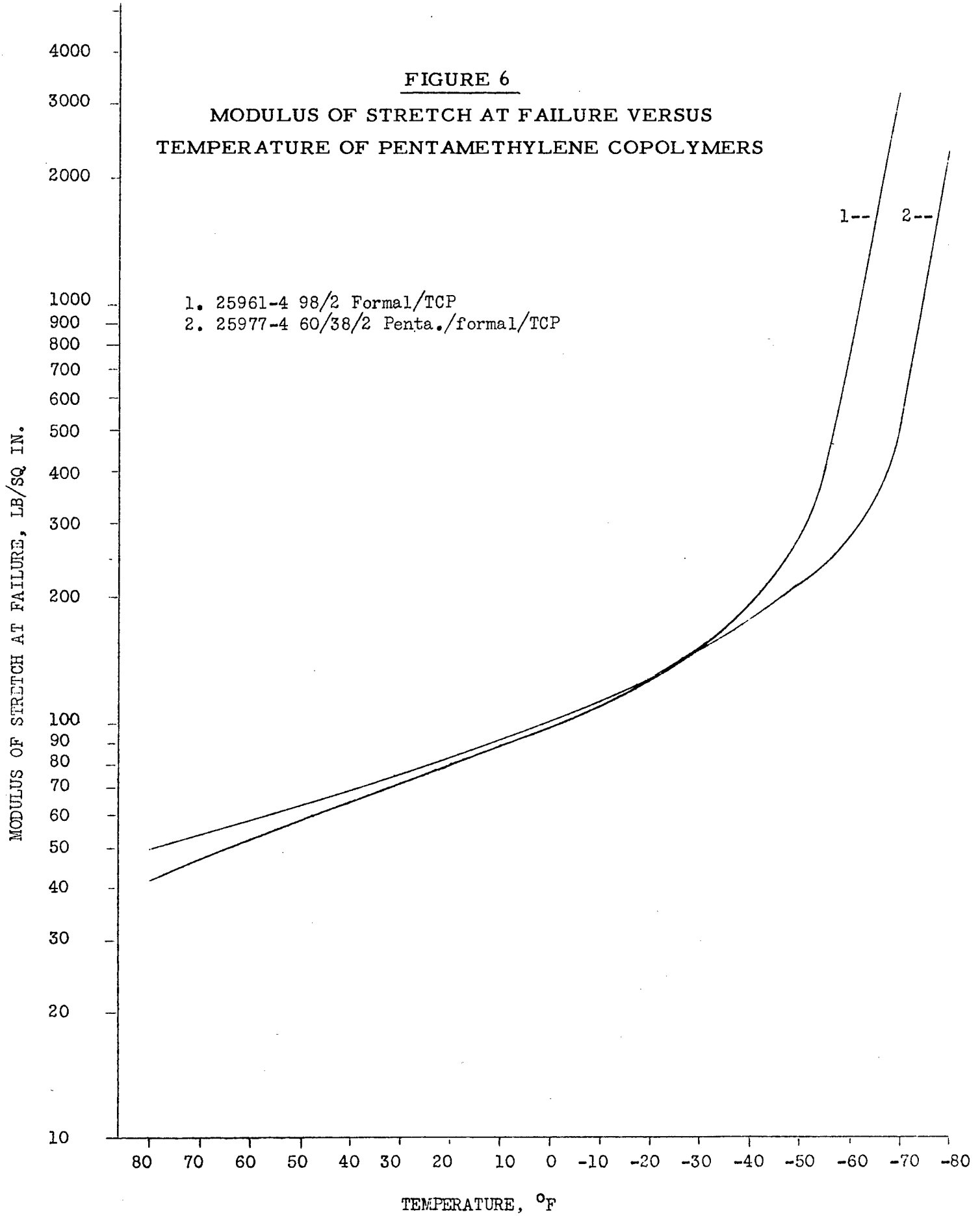


FIGURE 7

ULTIMATE TENSILE STRENGTH VERSUS TEMPERATURE OF ETHYLENE DICHLORIDE COPOLYMERS

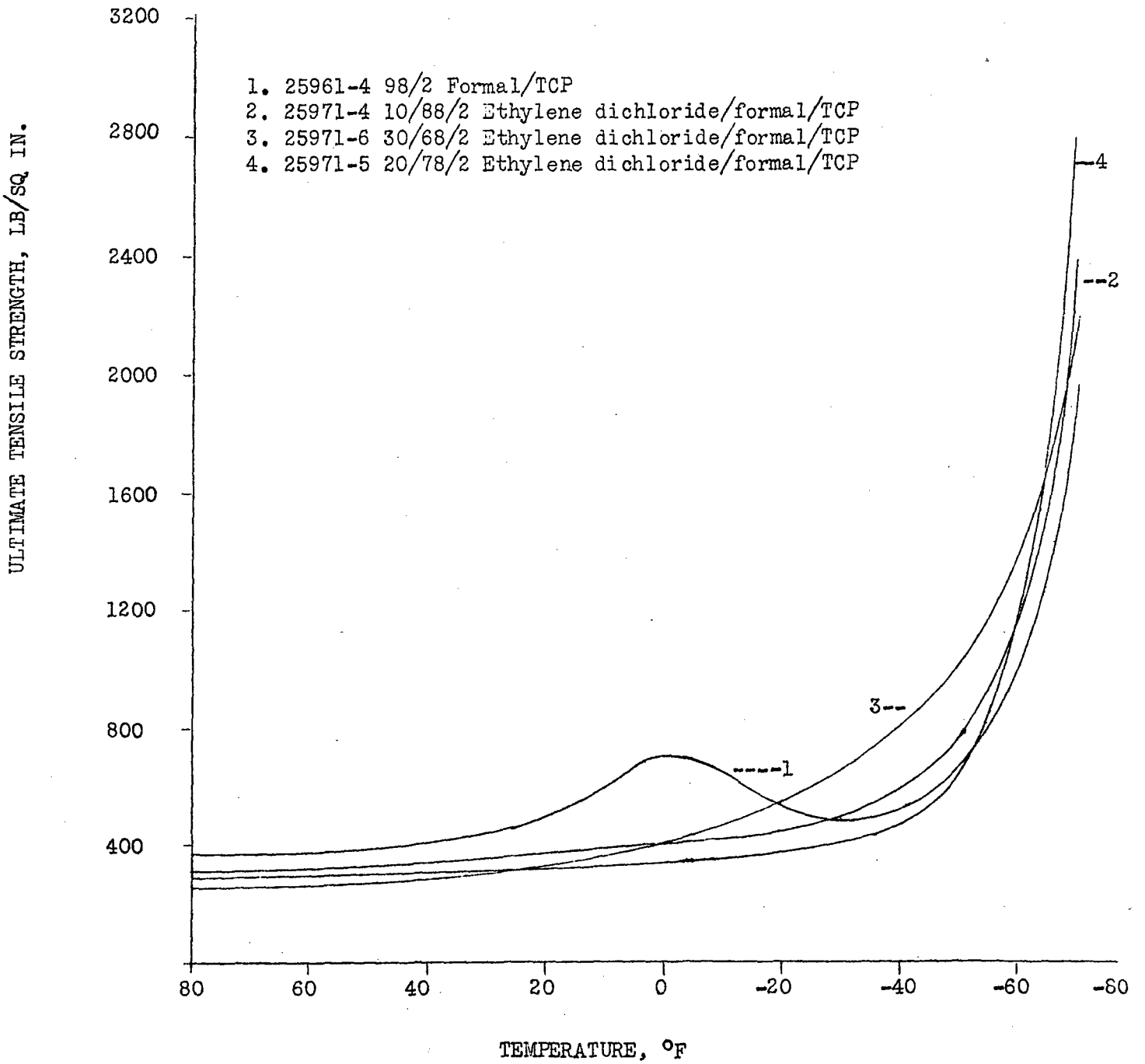


FIGURE 8

ULTIMATE ELONGATION VERSUS TEMPERATURE OF
ETHYLENE DICHLORIDE COPOLYMERS

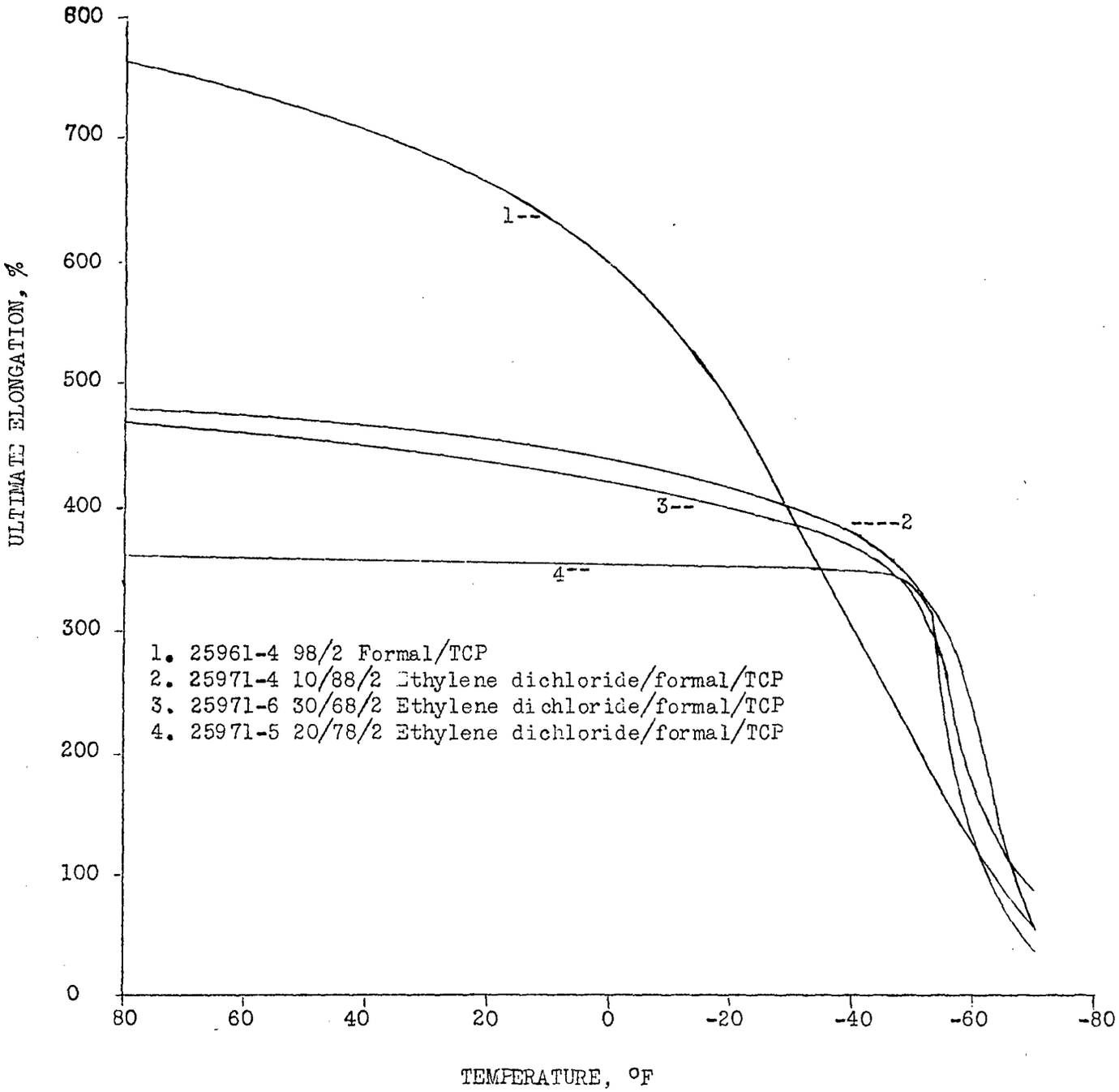


FIGURE 9

ABSOLUTE TORSIONAL MODULUS VERSUS TEMPERATURE

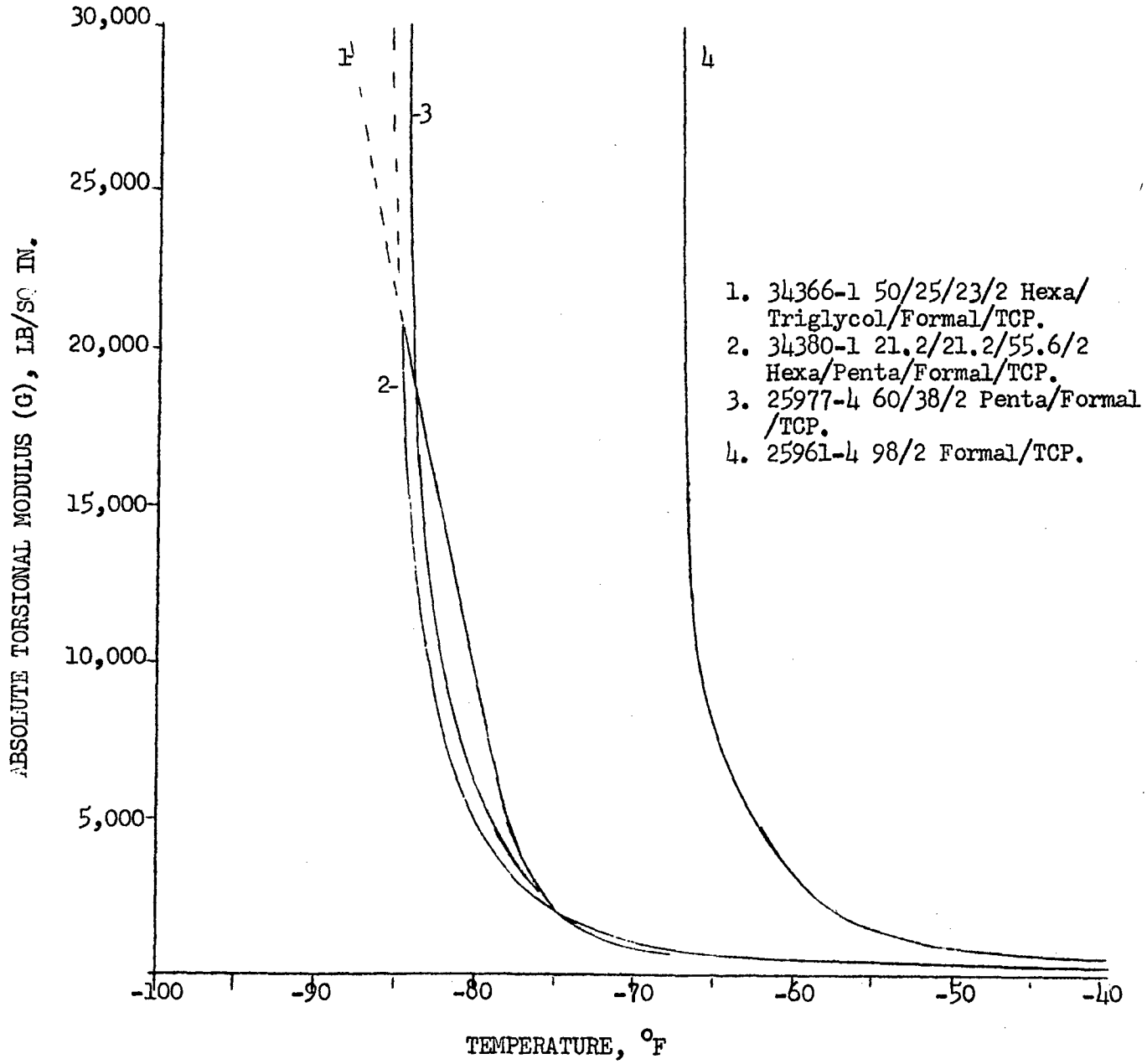
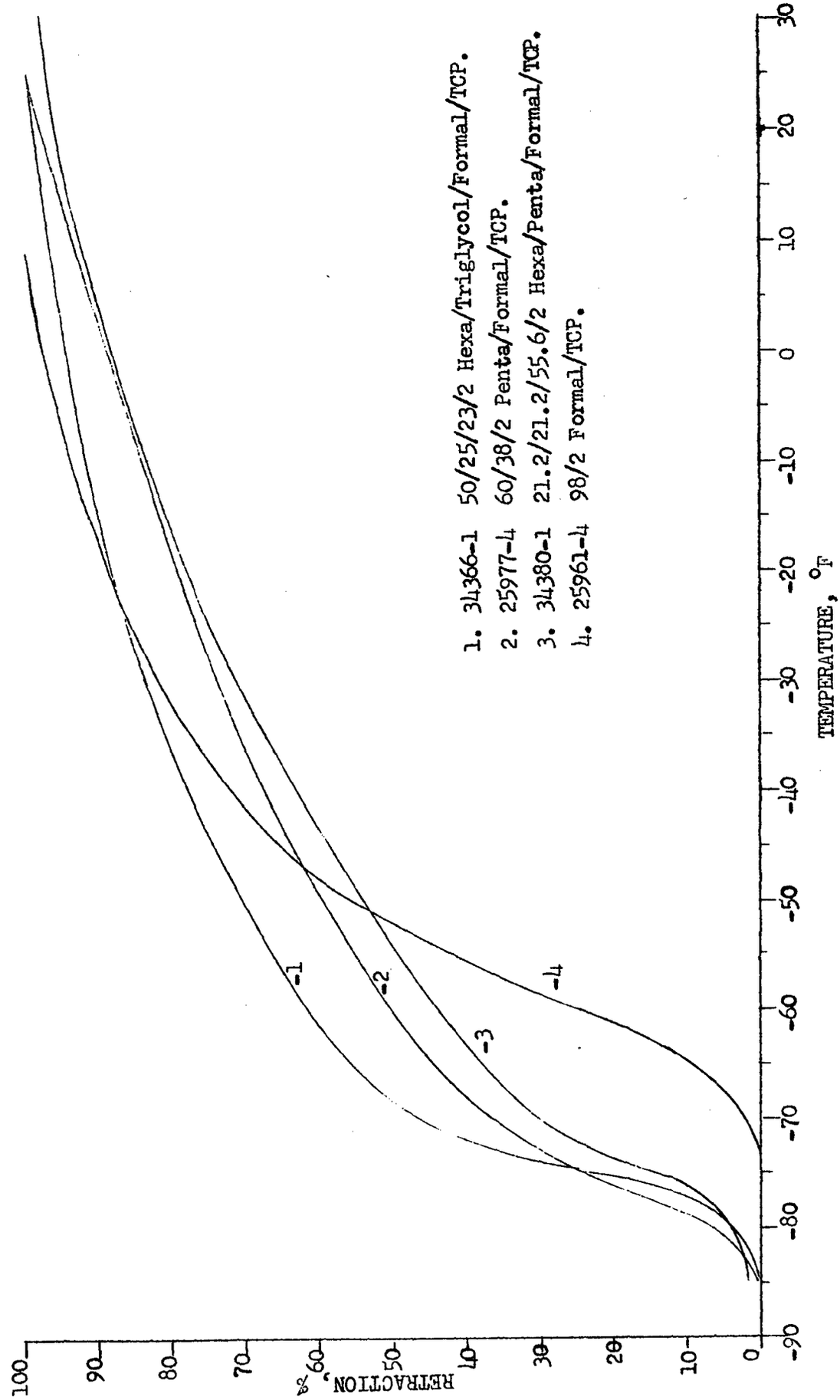


FIGURE 10

TENSION-RETRACTION VERSUS TEMPERATURE



II. DEVELOPMENT OF COMPOUNDING AND CURING METHODS

A. INTRODUCTION

This aspect of the program was undertaken to develop the optimum compounding and curing techniques for 'Thiokol' LP-2 and new experimental polymers. Thus, with pentamethylene dichloride/formal copolymer, an intensive study was conducted to determine the cause of excessive weight and volume loss upon heat aging this copolymer in the standard evaluation recipe.

The use of various additives was investigated in an attempt to enhance the adhesion and toughness of the various liquid polymers. These investigations involved the evaluation of adhesion additives, epoxide polymers to obtain clear and tough sealant compounds, inorganic fillers and miscellaneous polymers as reinforcing agents.

The employment of organic curing agents rather than lead peroxide and the development of room temperature curing systems with the new curatives was also investigated.

B. DEVELOPMENT OF HEAT AGING RESISTANCE IN PENTAMETHYLENE DICHLORIDE/FORMAL COPOLYMERS

1. Introduction

Although the pentamethylene/formal copolymers possessed superior low temperature properties, the apparent heat aging characteristics at 212°F of these compounds were extremely poor. Standard evaluation compounds containing pentamethylene dichloride/formal displayed a very high weight loss and decrease in volume during heat aging. The compounds also case hardened and cracked when flexed 180° after 72 hours of aging at 212°F. Therefore, an intensive investigation was undertaken to determine the cause of the poor heat aging characteristics and to develop better curing systems.

2. Decrease in Weight of Various Polymers During Heat Aging

As the first step in attacking this problem, equal weights of the following uncompounded polymers with a rank of 2.25 were aged in glass culture dishes for 216 hours at 212°F: 98/2 formal/TCP laboratory control, 60/38/2 pentamethylene dichloride/formal/TCP, and chain-stoppered 60/38/2 pentamethylene dichloride/formal/TCP. The formal polymer and the unstoppered pentamethylene/formal copolymer were also compounded in the evaluation formulation and aged in the same manner. Percentage weight loss, based on the weight of unaged polymer in the compound, was determined after 24, 48, 72, 144, 168 and 216 hours of heat aging.

The data in Table 22 and the curves in Figure 11 show that the weight losses of the three uncompounded polymers were low and comparable to one another.

However, the compounded pentamethylene/formal copolymer lost considerably more weight than did the compounded formal. These results showed that although the pentamethylene/formal copolymer had a lower viscosity, it was not inherently more volatile at 212°F than the formal polymer and that the curing agent and/or filler were responsible for the weight loss in both liquid polymers. In curing thiol terminated liquid polysulfide polymers with lead peroxide, the following mechanism of vulcanization is thought to occur:

$$\dot{H}S\text{-}R\text{-}SH + PbO_2 + HS\text{-}R\ SH \longrightarrow \text{-}S\text{-}R\text{-}SS\text{-}R\text{-}S\text{-} + Pb0 + H_20$$

$$HS\text{-}R\text{-}SH + PbO + HS\text{-}R\text{-}SH \longrightarrow \text{-}S\text{-}R\text{-}S\text{-}Pb\text{-}S\text{-}R\text{-}S\text{-} + H_2O$$

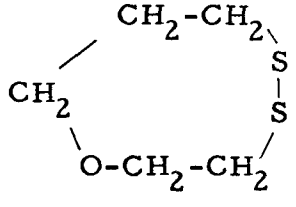
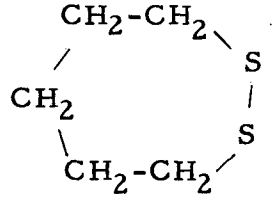
The -R-S-Pb-S-R- segments are subject to ionization and at elevated temperatures are susceptible to volatilization through the formation of cyclic disulfide ring compounds that are fairly volatile. The following reactions are believed to take place:

$$\ldots R\text{-}SS\text{-}R\text{-}SS\text{-}R\text{-}S\text{-}Pb\text{-}S\text{-}R\ldots \longrightarrow \ldots R\text{-}SS\text{-}R\text{-}SS\text{-}R\text{-}S^- + {}^+Pb\text{-}S\text{-}R\ldots$$

$$\ldots R\text{-}SS\text{-}R\text{-}SS\text{-}R\text{-}S^- \xrightarrow{heat} \ldots R\text{-}SS\text{-}R\text{-}S^- + R\begin{matrix}S\\|\\S\end{matrix}$$

$$\ldots R\text{-}SS\text{-}R\text{-}S^- \xrightarrow{heat} \ldots R\text{-}S^- + R\begin{matrix}S\\|\\S\end{matrix}$$

$$\ldots R\text{-}S^- + {}^+Pb\text{-}S\text{-}R\ldots \longrightarrow \ldots R\text{-}S\text{-}Pb\text{-}S\text{-}R\ldots$$

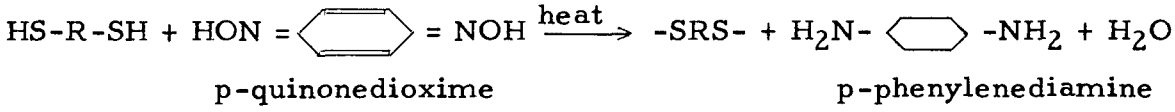
In the case of the formal polymer, it is believed that the cyclic formal disulfide,  , is formed. With the pentamethylene/formal copolymer, presumably both the pentamethylene disulfide and formal disulfide cyclic compounds are formed. The pentamethylene disulfide,  , a seven membered ring compound, is formed more easily than the cyclic formal disulfide, a nine membered ring. In confirmation of the foregoing mechanism, it was observed that pentamethylene/formal copolymer cured in the standard lead peroxide control formulation and subjected to dry distillation under vacuum at 85°C yielded a distillate identified as pentamethylene disulfide.

Since there are more thiol terminals per unit weight of polymer in low molecular weight polymers, more of the cyclic compounds should be formed during the heat aging of low molecular weight polymer compounds cured with lead peroxide than in those of higher molecular weight.

3. Effect of Compounding Ingredients and Curing Agents

To determine the effect of various types of fillers and curative systems on the resistance of thiol terminated liquid polymers to aging at 212°F, the 'Thiokol' LP-2 systems listed in Table 23 were investigated. 'Thiokol' LP-2 was used since there was no pentamethylene/formal copolymer available at the time and the data obtained with LP-2 should be indicative of what to expect with pentamethylene/formal copolymer. Weight loss and decrease in volume were determined after 24, 72, 144, 168 and 192 hours of aging at 212°F.

From the data in Table 23 and the curves in Figure 12, it is apparent that the weight loss of the compounds during aging at 212°F is a function of the type of curing agent and compounding materials used in the formulation. When LP-2 was compounded with zinc sulfide filler and cured with the GMF(p-quinonedioxime)-DPG(diphenylguanidine) system for 24 hours at 158°F, the weight loss was comparable to that of the uncompounded polymer. In this cure there is no possibility of the formation of metallic polymer 'salts' that can ionize to form volatile cyclic compounds; an oxidation reaction occurs in which p-phenylenediamine is one of the major products. Diphenylguanidine is used as an activator to provide the alkaline environment necessary for the cure. The general curing reaction is as follows:



p-quinonedioxime p-phenylenediamine

Substitution of 30 parts of SRF carbon black (Pelletex) for 50 parts of zinc sulfide in the lead peroxide control formulation substantially reduced the weight loss of the compound.

When the zinc sulfide was omitted from the control formulation, the weight loss of the rubber was only slightly reduced. However, when both the zinc sulfide and lead stearate were omitted, a substantial reduction in the weight loss of the cured compound during heat aging occurred. This indicates that the lead stearate accelerated the weight loss of the lead peroxide cured rubber and that the effect of the zinc sulfide on weight loss was quite inconsequential.

The addition of 0.25 part of sulfur per 100 parts of the LP-2 in the lead peroxide control formulation reduced significantly the weight loss of the rubber during heat aging. The presence of this quantity of sulfur in the compound presumably decreases the amount of the lead 'salt' in the polymer chain through the following mechanism:

Nevertheless, much of the lead 'salt' structure still remains in the cured polymer, which continues to form the volatile formal disulfide.

The weight loss of the rubbers during heat aging is accompanied by a decrease in volume of about the same magnitude. Generally, the physical properties of these LP-2 compounds were not greatly affected by aging for 72 hours at 212°F. This weight loss progresses after 72 hours of aging and in all probability a point is finally reached where the loss of polymer is sufficient to result in degradation of the physical properties of the rubber.

4. Effect of Fillers and Different Types of Curing Agents

Although the previous heat aging data indicated that Pelletex was superior to zinc sulfide as a filler in LP-2 compounds cured with lead peroxide, there are advantages in utilizing a white sealant formulation. Therefore, another commonly used white pigment, titanium dioxide, was compared with zinc sulfide in the lead peroxide control formulation and in the GMF-DPG cure for resistance to aging at 212°F. These fillers were compared on an equal weight basis.

From the data in Table 24 and the curves in Figure 13, the use of titanium dioxide appeared to be more desirable in the lead peroxide cure than zinc sulfide from the standpoint of heat aging resistance. However, in the GMF-DPG cure, the two fillers were comparable in this respect. The physical properties of the zinc sulfide and titanium dioxide compounds before and after aging for 72 hours at 212°F were in the same range.

5. Effect of Lead Peroxide, Sulfur and Viscosity

To obtain information concerning the effect of the quantity of lead peroxide and sulfur in the formulation and viscosity of the liquid polymer on the resistance of the cured rubbers to aging at 212°F, compounds containing zinc sulfide, lead stearate and lead peroxide were studied.

Doubling the amount of lead stearate and lead peroxide in the LP-2 control formulation resulted in a cured compound with a slightly lower weight loss and decrease in volume during aging at 212°F than the cured control compound (see Table 25 and Figure 14). The physical properties of the unaged samples and those that were aged for 72 hours at 212°F were in the same range.

Incorporation of 0.5 part of sulfur per 100 parts of LP-2 in the control formulation greatly reduced the decrease in weight and volume of the rubber during heat aging. In this respect, results comparable to those with the GMF-DPG cure were obtained.

To evaluate the effect of viscosity of the liquid polymer on resistance to heat aging, LP-3 compound No. 34307-5 was studied. Since the viscosity of LP-3 is much lower than that of LP-2, it was necessary to incorporate twice the amount of lead peroxide used in the control formulation and sulfur to obtain a satisfactory cure. The resultant polymer decreased considerably more in weight and volume during heat aging than did LP-2 compound without sulfur. This observation supports the assumption relative to the mechanism of the weight loss of lead peroxide cured liquid polymer compounds, namely, that the greater number of thiol

terminals present in LP-3 results in the formation of a greater number of volatile R-S-Pb-S-R segments.

6. Effect of Curing Agents on the Resistance of Pentamethylene/Formal Compounds to Heat Aging

Since the LP-2 compounds cured by the GMF-DPG system possessed excellent heat aging characteristics at 212°F, the next logical step was to investigate the heat aging characteristics of the pentamethylene/formal copolymer cured with this system. Although the viscosity of the pentamethylene/formal copolymer sample used here was much lower than that of LP-2, it was decided to conduct several aging studies, since an effective cure with a copolymer of low viscosity would be applicable to those of higher viscosity. Accordingly, formulations containing zinc sulfide in conjunction with lead stearate and lead peroxide or GMF-DPG were studied. Because of its comparatively low molecular weight, the pentamethylene/formal copolymer required more curing agent for a satisfactory cure than did LP-2.

It is apparent from the data in Table 26 and the curves in Figure 15 that pentamethylene/formal copolymers cured by the GMF-DPG system displayed excellent heat aging characteristics, whereas those cured with lead peroxide had poor resistance to heat aging. Incorporation of 0.25 part of sulfur in the lead peroxide formulation greatly reduced the weight loss during heat aging, but not sufficiently to prevent excessive shrinkage and embrittlement of the rubber. Because of this embrittlement, the physical properties of the pentamethylene/formal copolymers cured with lead peroxide, which were aged for 72 hours at 212°F, could not be determined.

It should be pointed out that too much GMF was used in curing the pentamethylene/formal copolymer compound No. 30160-3. The decrease in hardness of this rubber after 72 hours of aging was undoubtedly caused by a slight reversion of the polymer.

A sample of 60/38/2 pentamethylene/formal/TCP copolymer with a rank of 2.25 and of a higher viscosity than the preceding sample (745 versus 35 poises) was prepared and compounded in the control formulation and with the curing systems developed for improved resistance to heat aging.

From the hardness data recorded in Table 27, it is apparent that the pentamethylene/formal copolymer was undercured in the standard evaluation formulation. A better cure was obtained when 15 parts of lead peroxide and 2.8 parts of lead stearate were used. With this formulation, this pentamethylene/formal copolymer of higher molecular weight did not decrease in volume and weight to as great an extent as did the lower molecular weight copolymer shown in Table 26. The pentamethylene/formal compounds cured with the lead peroxide-lead stearate system were less resistant to heat aging than the formal control compound. The former case hardened and cracked when flexed 180° after 24 and 48 hours of aging at 212°F; this did not occur with the formal control even after 216 hours of aging.

According to the results, the following curing systems yielded rubbers with the pentamethylene/formal copolymer that decreased very little in weight and volume and did not crack when flexed after 216 hours of heat aging:

a. Lead peroxide/lead stearate/0.25 part sulfur/maleic anhydride.
b. GMF/triethanolamine/sulfur.
c. Lead peroxide/lead stearate/0.5 part sulfur.

The three cures were comparable with respect to decrease in weight and volume and increase in hardness during heat aging.

C. ADDITIVES

1. Additives for Imparting Adhesion

The use of one part of maleic anhydride or furoic acid per 100 parts of LP-2 in conjunction with 0.5 part Bakelite resin BRR-18794 in the control formulation resulted in good adhesion to aluminum at room temperature. The compound containing maleic anhydride and BRR-18794 was evaluated for stress-strain, adhesion and low temperature torsional stiffness properties. The data in Table 28 indicate that the use of these materials resulted in poorer stress-strain properties but had no effect on low temperature torsional stiffness and gave excellent adhesion to aluminum. A slight undercure may have been responsible for the poorer physical properties and poorer resistance to SR-6 and SR-10 fuels.

Additional studies were conducted with maleic anhydride and furoic acid in the LP-2 control formulation to determine the optimum concentrations required to achieve a good balance between a satisfactory 'pot' life of the compound and adhesion properties. Preliminary tests indicated that in quantities necessary to obtain adhesion, the use of maleic anhydride retarded the cure, whereas with furoic acid acceleration of the cure occurred. Therefore, these materials were evaluated separately and in combinations. A working life of approximately 1.5 hours and excellent adhesion to aluminum at room temperature were obtained with a combination of 0.25 part each of furoic acid and maleic anhydride per 100 parts of LP-2 (see Table 29).

Tests were conducted on the 'Thiokol' LP-2 compounds listed in Table 30 to determine the effect of sulfur and maleic anhydride on compression set properties at 158° and -40°F. These compounds were cured to comparable hardness at 80°F and 55% to 60% relative humidity.

It is apparent from the data in Table 30 that the compression set resistance of the rubber at 158°F was markedly improved by the use of sulfur alone or in conjunction with maleic anhydride. The use of sulfur alone did not affect the compression set at -40°F, but together with the adhesion additive resulted in an improvement in this property.

2. Inorganic Fillers

a. Calcined Magnesia

Since it was indicated from studies conducted on another problem dealing with liquid polymers that a small quantity of calcined magnesia increased toughness, this material was evaluated in the control formulation. Two compounds were prepared: one contained 2 parts of extra light calcined magnesia per 100 parts of LP-2 in addition to the zinc sulfide filler; in the other compound, 25% of the zinc sulfide filler was replaced with the calcined magnesia. The data in Table 31 indicate that this filler had a negligible effect on increasing the toughness.

b. Micro Mica (C-3000)

The zinc sulfide filler in the control formulation was replaced with this extremely fine particle size mica to evaluate its effect on the toughness of the compound. From the tensile and tear strengths and elongation it is evident that the mica filler was not as reinforcing a pigment as zinc sulfide (see Table 31).

3. Miscellaneous Polymers

a. Polyester Polymers

A special maleic alkyd polyester, Paraplex 5-B, and a sebacic acid type polyester, Paraplex B-20, were evaluated as additives for improving the adhesion of LP-2 to aluminum. Incorporation of the maleic alkyd polyester and the sebacic acid type polyester into the LP-2 did not improve the toughness and adhesion to aluminum (see Table 32). Their use resulted in poorer resistance to volume change in SR-6 and SR-10 fuels and slightly poorer low temperature flexibility.

b. Phenolic Resins

'Thiokol' LP-2 was compounded with a phenolic resin and an oil modified phenolic, Bakelite resin BK 3962, with the objective of enhancing the adhesion and toughness characteristics. Since the phenolic resin in the LP-2 compound produced a very soft cure, it was considered unsuitable for this use. No improvement in toughness was gained by incorporating the oil modified phenolic (see Table 32). This resin reduced the low temperature flexibility and resistance to compression set of the LP-2 compound.

c. Vinyl Chloride Type Polymer

An attempt was made to incorporate a relatively high molecular weight vinyl chloride type polymer into LP-2 for the purpose of improving the toughness and possibly the adhesion properties. This additive was incompatible with LP-2 and was considered unsatisfactory for this application.

d. Nylon Polymers

Two Nylon polymers that were claimed to possess excellent adhesive properties, high strength, and low brittleness temperature and to be highly resistant to aromatic and aliphatic hydrocarbons were tested as additives. Both samples of Nylon were incompatible with LP-2. It does not appear at this time that they can be utilized in this application.

4. Reaction Products with Methylene-Bis-Acrylamide

The possibility of obtaining reaction products with 10/88/2 bis(2-chloroethylamine)/formal/TCP, 10/88/2 N-methyl dichlorodiethylamine/formal/TCP copolymers and 'Thiokol' LP-2 with methylene-bis-acrylamide, CH_2= CHOCHN-CH_2-NHCOCH=CH_2, that would be suitable for use as clear sealant compounds was investigated. Formulations containing 10 and 50 parts of methylene-bis-acrylamide per 100 parts of polymer were prepared and cured at 77° and 212°F. None of the compounds cured at 77°F, but cures were obtained with all of the formulations at 212°F. Translucent, rubbery and 'short' materials were obtained with the formulations containing 10 parts of methylene-bis-acrylamide per 100 parts of polymer. The formulations containing 50 parts of the additive gave opaque, fairly tough but 'short' materials. None of these compounds appeared to be suitable for clear sealant compounds.

D. CURING SYSTEMS

1. Organic Curing Agents

Several formulations were prepared with LP-2 liquid polymer utilizing the organic catalyst cumene hydroperoxide and diphenyl and triphenylguanidine as activators in an attempt to obtain a satisfactory curing mechanism and material for a clear sealant compound. According to the data in Table 33 no satisfactory cures were obtained. In general, the working life (set time) of the compounds was extremely short and the stocks obtained after 96 hours of cure at room temperature were soft and weak.

2. Development of Room Temperature Cures

In view of the data obtained in the foregoing heat aging studies, it was quite apparent that the lead peroxide control formulation could not be used with the pentamethylene/formal copolymer to develop satisfactory resistance to heat aging at 212°F. Although the resistance to heat aging of a pentamethylene copolymer in the molecular weight range of LP-2 was not established, it was deemed advisable to proceed with the development of a new cure since the GMF-DPG system did not cure liquid polymers within 24 hours at 77°F.

About 45 different cure combinations were evaluated with LP-2 liquid polymer for application to other thiol terminated polymers. Of these, the systems listed in Table 34 showed the most promise for curing LP-2 at 77°F and 55 to 60% relative humidity in 24 hours. Aging studies were conducted only on some of the

compounds (No. 25999-6, 38651-3, 38656-3 and 38656-6 which developed good cures.

The compounds utilizing zinc chromate or potassium dichromate plus GMF (No. 25999-6 and 38651-3) displayed poor heat aging characteristics at 212°F. They decreased considerably in weight and volume and increased markedly in hardness after 120 and 144 hours of heat aging and the specimens cracked when flexed 180°.

The heat aging results for compounds No. 38656-3 and 38656-6 (lead peroxide/sulfur/maleic anhydride and GMF/triethanolamine/sulfur, respectively), recorded in Table 35, indicate that the decrease in weight and volume of these compounds during heat aging was considerably less than that of the control compound No. 34307-1. The physical properties of these compounds were not degraded after aging for 72 hours at 212°F nor did they crack when flexed 180° after 216 hours at 212°F. The two new cures are far superior to the standard cure with respect to decrease in weight and volume during aging at 212°F.

E. POLYVINYL CHLORIDE - 'THIOKOL' WD-2 LATEX SYSTEM

A few latex compositions were prepared with a polyvinyl chloride type latex, Geon Latex No. 652, and softened WD-2 latex. The WD-2 latex was softened by heating at 180°F for 1 hour with 1.25% (based on weight of latex solids) ethyl Tuads. The Geon latex was added to the filtered, softened WD-2 latex by means of agitation. Films were applied to aluminum test panels and examined for continuity, toughness and adhesion properties. Although the films appeared to be homogeneous and continuous when examined with a magnifying glass, the incorporation of the polyvinyl chloride type polymer into the WD-2 polymer did not increase the toughness or adhesion characteristics of the WD-2.

TABLE 22

DECREASE IN WEIGHT OF VARIOUS POLYMERS DURING HEAT AGING AT 212°F

Compound No.	25281-3	25281-2	25281-1	25281-4	30159-1
	Uncompounded			Compounded	
98/2 Formal/TCP (No. A194374, 1400 poises)	100	--	--	100	--
60/38 Penta./Formal/TCP (No. A19444R1, 200 poises)	--	100	--	--	100
Chain stoppered 60/38/2 Penta./Formal/TCP (No. A29455A1, 410 poises)	--	--	100	--	--
Zinc sulfide (ZS-800)	--	--	--	50	50
Lead stearate	--	--	--	1.4	1.4
Lead peroxide	--	--	--	7.5	7.5
Weight loss after aging at 212°F, %					
24 hr.	1	3	1	14	24
48 hr.	2	4	1	21	34
72 hr.	3	4	1	26	44
144 hr.	4	3	3	34	--
168 hr.	4	4.5	3.5	35	58
216 hr.	5	5	4.5	39	72

TABLE 23

EFFECT OF COMPOUNDING INGREDIENTS AND CURING AGENTS ON THE RESISTANCE OF 'THIOKOL' LP-2 TO HEAT AGING AT 212°F

Compound No.	25987-6	25987-2	25990-4[a]	25987-1	25987-5	25987-4	25987-3
	Uncompounded	Control Compound					
LP-2 (Lot 387, 460 poises)	100	100	100	100	100	100	100
Zinc sulfide (ZS-800)	--	50	50	--	50	--	--
Pelletex (SRF)	--	--	--	30	--	--	--
Lead stearate	--	1.4	--	1.4	1.4	1.4	--
Lead peroxide	--	7.5	--	7.5	7.5	7.5	7.5
Sulfur	--	--	--	--	0.25	--	--
p-Quinonedioxime	--	--	3	--	--	--	--
Diphenylguanidine	--	--	1	--	--	--	--
Vulcanizate Properties (Cured 24 hr. @ 77°F)							
		b/c	b/c	b/c	b/c	b/c	b/c
Shore hardness	--	48/53	43/43	54/57	48/50	38/40	37/38
100% Modulus, lb/sq in.	--	200/175	125/150	200/275	160/175	175/110	160/135
300% Modulus, lb/sq in.	--	375/375	360/350	475/725	325/--	--	--
Tensile strength, lb/sq in.	--	475/400	435/335	710/835	375/310	175/110	160/150
Elongation, %	--	375/255	350/315	460/345	300/275	240/145	195/190
Tear strength, lb/in.	--	25/27	22/25	115/143	26/24	10/11	10/11
Weight/volume loss after aging at 212°F, %							
24 hr.	--	11/10	2/2	9/7	8/8	10/17	8/8
72 hr.	2/--	22/13	3/3	15/12	16/14	20/27	16/16
144 hr.	2.5/--	27/24	4/4	18/16	18/16	25/31	20/21
168 hr.	3/--	28/25	4/3	19/16	20/19	26/32	22/22
192 hr.	--	30/25	4/4	20/16	22/19	28/33	22/23

a Cured 24 hours at 158°F.
b Unaged.
c Aged for 72 hours at 212°F.

TABLE 24

EFFECT OF FILLERS AND CURING AGENTS ON THE RESISTANCE OF 'THIOKOL' LP-2 COMPOUNDS TO HEAT AGING AT 212°F

Compound No.	25990-3	25990-1	25990-4[a]	25990-2[a]
LP-2 (Lot 387, 460 poises)	100	100	100	100
Zinc sulfide (ZS-800)	50	--	50	--
Titanium dioxide	--	50	--	50
Sulfur	--	--	--	--
Lead stearate	1.4	1.4	--	--
Lead peroxide	7.5	7.5	--	--
p-Quinonedioxime	--	--	3	3
Diphenylguanidine	--	--	1	1
Vulcanizate Properties (Cured 24 hr. @ 77°F)				
	b/c	b/c	b/c	b/c
Shore hardness	43/53	47/53	43/43	43/44
100% Modulus, lb/sq in.	150/225	160/200	125/150	125/150
300% Modulus, lb/sq in.	350/450	325/375	360/350	300/360
Tensile strength, lb/sq in.	550/525	635/510	435/335	425/460
Elongation, %	490/365	685/465	350/315	510/375
Tear strength, lb/in.	32/52	45/57	22/25	35/30
Weight/volume loss after aging at 212°F, %				
24 hr.	9.0/8	6.5/5	2/2	2/1
72 hr.	18/16	15/2	3/3	2/2
144 hr.	29/25	19/16	4/4	2.5/2
168 hr.	32/28	21/17	8/3	3/2
192 hr.	34/29	23/18	4/4	3/3

a Cured for 24 hours at 158°F.
b Unaged.
c Aged for 72 hours at 212°F.

TABLE 25

EFFECT OF AMOUNT OF LEAD PEROXIDE AND VISCOSITY ON THE RESISTANCE OF 'THIOKOL' LIQUID POLYMER TO HEAT AGING AT 212°F

Compound No.	34307-1	34307-2	34307-3	34307-5
	LP-2 Control Compound	LP-2	LP-2	LP-3
LP-2 (Lot 387, 460 poises)	100	100	100	--
LP-3 (7-21 poises)	--	--	--	100
Zinc sulfide (ZS-800)	50	50	50	50
Lead stearate	1.4	2.8	1.4	2.8
Lead peroxide	7.5	15.0	7.5	15.0
Sulfur	--	--	0.5	0.5
Vulcanizate Properties (Cured 24 hr. @ 77°F)				
	a/b	a/b	a/b	a/b
Shore hardness	48/53	50/52	48/53	53/51
100% Modulus, lb/sq in.	160/150	175/160	155/175	200/210
300% Modulus, lb/sq in.	360/325	375/350	360/400	425/450
Tensile strength, lb/sq in.	440/340	410/460	425/560	600/525
Elongation, %	400/325	440/500	360/470	460/380
Tear strength, lb/in.	37/39	37/45	46/55	66/62
Weight/volume loss after aging at 212°F, %				
24 hr.	9/7	6/4	2/0	10/9
48 hr.	12/10	10/6	2/1	14/12
72 hr.	15/13	13/11	3/2	18/15
144 hr.	22/20	18/14	4/3	26/14
168 hr.	24/21	19/16	5/3	28/23
216 hr.	28[c]/24	21[c]/17	6[c]/5	32[c]/26

a Unaged.
b Aged for 72 hours at 212°F.
c Specimens did not crack when flexed 180°.

TABLE 26

EFFECT OF CURING AGENTS ON THE RESISTANCE OF 'THIOKOL' LP-2 AND PENTAMETHYLENE/FORMAL COPOLYMER OF LOW VISCOSITY TO HEAT AGING AT 212°F

Compound No.	25990-3	25990-4	30160-2	30160-1	30160-3[a]
	LP-2 Control				
LP-2 (Lot 387, 460 poises)	100	100	--	--	--
60/38/2 Penta/formal/TCP (A29556 H1-2,35 poises)	--	--	100	100	100
Zinc sulfide (ZS-800)	50	50	50	50	50
Lead stearate	1.4	--	2.8	2.8	--
Lead peroxide	7.5	--	15	15	--
Sulfur	--	--	--	0.25	--
p-Quinonedioxime	--	3	--	--	5
Diphenylguanidine	--	1	--	--	1.5
Vulcanizate Properties (Cured 24 hours @ 77°F)					
	b/c	b/c	b/c	b/c	b/c
Shore hardness	43/53	43/43	37/d	53/d	52/46
100% Modulus, lb/sq in.	150/225	125/150	150/d	125/d	150/150
300% Modulus, lb/sq in.	350/450	360/350	150/d	200/d	325/--
Tensile strength, lb/sq in.	550/525	435/335	150/d	410/d	375/275
Elongation, %	490/365	350/315	950/d	955/d	375/270
Tear strength, lb/in.	32/52	22/25	57/d	69/d	25/23
Weight/volume loss after aging at 212°F, %					
24 hr.	9/8	2/2	31/26	25/22	4/3
48 hr.	14/12	--	50/40	35/30	5/4
72 hr.	18/16	3/3	70/55	43/37	5/5
144 hr.	29/25	4/4	--	60/51	7/6
168 hr.	32/28	4/3	--	63/54	7/6
192 hr.	--	4/4	--	--	--
216 hr.	36/31	--	--	69/60	9/7

a Cured for 24 hours at 158°F.
b Unaged.
c After aging for 72 hours at 212°F.
d The aged specimen could not be tested since it shrank, hardened and broke when flexed 180°.

TABLE 27

EFFECT OF CURATIVES ON HEAT AGING CHARACTERISTICS AT 212°F OF PENTAMETHYLENE/FORMAL COPOLYMER OF SATISFACTORY VISCOSITY

Compound No.	38663-1	34361-1	34361-2	34361-3	34361-4	34361-5
	LP-2 Control					
LP-2 (Lot 387, 460 poises)	100	--	--	--	--	--
60/38/2 Penta./Formal/TCP (A55253V) (745 Poises)	--	100	100	100	100	100
Zinc sulfide (ZS-800)	50	50	50	50	50	50
Lead stearate	1.4	1.4	1.4	--	1.4	2.8
Lead peroxide	7.5	7.5	7.5	--	7.5	15.0
Sulfur	--	--	0.25	0.5	0.5	--
Triethanolamine	--	--	--	3.0	--	--
p-Quinonedioxime	--	--	--	3.0	--	--
Maleic anhydride	--	--	1.0	--	--	--
Vulcanizate Properties (Cured 24 hr. @ 77°F)						
Shore hardness						
Unaged	50	23	48	42	46	43
After 216 hrs. 212°F	58	52	55	50	51	60
Weight/volume loss on aging at 212°F, %						
24 hr.	12/10	12/10	3/3	3/3	4/4	21[a]/19
48 hr.	19/17	26/22	4/4	4/3	4/4	--
72 hr.	24/19	33/28	5/4	4/4	5/4	38/33
144 hr.	30/25	43/26	7/6	4/4	6/5	43/38
168 hr.	32/27	44/38	8/7	4/4	6/5	49/43
216 hr.	34/29	46/40	9/7	4/4	7/6	51/45

a Specimen cracked on surface when flexes 180°.

TABLE 28

EFFECT OF ADHESION ADDITIVES ON PROPERTIES OF LP-2 POLYMER (LOT 370)

(Compounded by Standard Evaluation Recipe, Appendix B, plus Additives Shown)

Compound No.		AV. LP-2 Control	28118-3
		No Additives	
Maleic anhydride		--	1
BRR-18794		--	0.5
	Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]		
		b/c	b/c
Shore hardness		48/52	52/55
100% Modulus, lb/sq in.		140/170	210/200
300% Modulus, lb/sq in.		340/300	--
Tensile strength, lb/sq in.		610/620	430/600
Elongation, %		580/640	220/260
Tear strength, lb/in.		49/48	39/51
Compression set, %			
At 1 hour			
158°F		78	58
-40°F		40	10
Torsional test			
Relative modulus			
T_5, -°F		50/46	48/50
T_{10}		54/52	54/53
T_{50}		63/60	65/60
T_{100}		65/61	67/62
Absolute modulus			
G_{rt}, lb/sq in.		150/113	170/223
$G_{5,000}$, -°F		61/59	60/57
$G_{10,000}$		65/62	65/60
$G_{20,000}$		68/65	68/62
Swelling volume, %			
SR-6	1 day	12	8
	1 month	-2	14
SR-10	1 day	1	1
	1 month	-4	17
Adhesion, lb/in.			
After 24-hr. cure		Poor	15[d]
After 48-hr. in SR-6		Poor	20-25[d]

a Unless indicated otherwise, the specimens were unaged.

b Unaged.

c Aged for 72 hours at 212°F.

d Adhesive strength stronger than cohesive strength of material. Fabric separated from stock.

TABLE 29

EFFECT OF ADDITIVES ON CURE AND ADHESION PROPERTIES OF 'THIOKOL' LP-2 (LOT 386)

(Compounded by Standard Evaluation Recipe, Appendix E, Plus Additives Shown)

Compound No.	28142-1	28142-2	28142-3	28142-4	28142-5	28142-6
Maleic anhydride	--	--	0.25	0.50	1.0	1.0
Furoic acid	--	0.25	0.25	0.25	0.25	--
'Pot' life[a]	3 hr. 40 min.	50 min.	1 hr. 30 min.	1 hr. 30 min.	1 hr. 20 min.	2 hr. 10 min.
Shore hardness						
At 4 hours	14	46	40	35	30	--
At 16 hours	45	46	48	46	46	--
At 24 hours	45	48	48	46	46	--
At 48 hours	45	50	50	46	46	--
Adhesion[b]						
At 4 hours	Poor	Excellent	Excellent	Excellent	Excellent	Poor
At 16 hours	"	"	"	"	"	"
At 24 hours	"	"	"	"	"	"
At 48 hours	"	"	"	"	"	"

a At room temperature.

b Compound spread on aluminum panel cleaned with VM and P Naphtha and evaluated for adhesion after each cure interval by scraping with a knife.

TABLE 30

EFFECT OF SULFUR AND MALEIC ANHYDRIDE ON THE RESISTANCE OF 'THIOKOL' LP-2 TO COMPRESSION SET

Compound No.	38674-1	38674-2	38674-3	38683-3
	Control			
LP-2 (Lot No. 387)	100	100	100	100
Zinc sulfide (ZS-800)	50	50	50	50
Lead stearate	1.4	1.4	1.4	1.4
Lead peroxide	7.5	7.5	7.5	7.5
Sulfur	--	0.25	0.25	--
Maleic anhydride	--	--	1.00	1.00
	Vulcanizate Properties (Cured @ 77°F)			
Shore hardness	52	52	50	Did not cure
Compression set, %				
At 1 hour				
158°F	75	38	47	--
-40°F	33	32	23	--

TABLE 31

EFFECT OF ADDITIVES ON PROPERTIES OF LP-2 POLYMER

Compound No.	Av. LP-2 Control	28123-1	28130-3	28130-1
	No Additives			
LP-2 (Lot 370)	100	100	100	100
Zinc sulfide (ZS-800)	50	50	37.5	--
Ex. light calcined magnesia	--	2	12.5	--
Micro Mica (C-3000)	--	--	--	50
Lead stearate	1.4	1.4	1.4	1.4
Lead peroxide	7.5	7.5	7.5	7.5
	Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]			
	b/c	b/c	b/c	b/c
Shore hardness	48/52	48/53	53/58	61/67
100% Modulus, lb/sq in.	140/170	140/190	225/225	375/--
300% Modulus, lb/sq in.	340/300	360/440	500/525	--
Tensile strength, lb/sq in.	610/620	710/640	610/590	375/350
Elongation, %	580/640	570/480	420/350	100/90
Tear strength, lb/in.	49/48	54/60	61/65	34/37
Compression set, %				
At 1 hour				
158°F	78	97	77	87
-40°F	40	32	29	36

a Unless indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.

TABLE 32

EFFECT OF ADDITIVES ON PROPERTIES OF LP-2 POLYMER

Polymer No.	Av. LP-2 Control	28102-1	28108-1	28108-2
LP-2 (Lot 310)	100	100	100	100
Zinc sulfide (ZS-800)	50	50	50	50
Polymer BRR-18794	--	--	--	--
Bakelite				
BK 3962 (51% solids)	--	19.6	--	--
Paraplex 5-B	--	--	10	--
Paraplex G-20	--	--	--	10
Lead stearate	1.4	1.4	1.4	1.4
Lead peroxide	7.5	7.5	7.5	7.5
Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]				
	b/c	b	b/c	b/c
Shore hardness	48/52	48	50/57	48/60
100% Modulus, lb/sq in.	140/170	200	150/210	150/225
300% Modulus, lb/sq in.	340/300	340	260/375	260/375
Tensile strength, lb/in.	610/620	490	490/450	425/410
Elongation, %	580/640	500	650/460	580/440
Compression set, %				
At 1 hr.				
180°F	95	104	97	98
158°F	78	100	90	94
-20°F	32	49	53	41
-40°F	40	55	54	56
Torsional test				
Relative modulus				
T_5, -°F	50/46	44	16	44
T_{10}	54/52	53	52	52
T_{50}	63/60	61	61	62
T_{100}	65/61	62	63	63
Absolute modulus	b/c			
G_{rt}, lb/sq in.	150/113	166	168	206
$G_{5,000}$, -°F	61/59	59	59	59
$G_{10,000}$	65/62	61	62	61
$G_{20,000}$	68/65	63	64	--

(Table continued and footnotes on next page.)

TABLE 32 (Contd.)

Polymer No.		Av. LP-2 Control	28102-1	28108-1	28108-2
Swelling volume, %					
SR-6	1 day	12	7	20	15
	2 weeks	2	7	23	11
SR-10	1 day	1	5	11	6
	2 weeks	-2	-5	18	14
Adhesion					
After 24-hr. cure		Poor	--	Poor	Poor
After 48-hr. immersion in SR-6		Poor	--	Poor	Poor

a Unless indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.

TABLE 33

CURE STUDIES OF LP-2 LIQUID POLYMER WITH ORGANIC CURING AGENTS

Compound No.	25276-1	25276-2	25276-3	25276-4	25276-5	25277-1	25277-4	25277-2	25277-3	25277-5
LP-2	100	100	100	100	100	100	--	100	100	100
Cumene hydroperoxide (70%)	5.0	7.0	5.0	5.0	7.0	7.0	7.0	7.0	5.0	7.0
Diphenylguanidine (20%)	1.0	3.0	--	--	3.0	1.4	1.4	1.4	--	1.4
Triphenylguanidine (20% soln.)	--	--	1.0	1.4	--	--	--	--	1.4	--
Epoxide polymer BRR-18794	--	--	--	--	--	--	--	--	--	5.0
LP/amine	--	--	--	--	--	--	--	--	--	5.0
Epoxide polymer RN-45	--	--	--	--	4.0	--	--	4.0	4.0	--
Set time, min.	20	2	24 hr.	70	6	10	10	8	2 hr.	13
Shore hardness										
At 24 hr.	0	8	0	0	20	16	30	12	0	6
At 96 hr.	0	8	0	0	20	18	30	13	0	6
Remarks[a]	Extensible and weak	'Short' and weak	Very soft and tacky	Extensible and weak	'Short' and cheesy	--	Weak and 'short'	Weak and 'short'	Very soft and tacky	Weak and 'short'

a Visual and manual examination after 96 hours of cure at room temperature.

TABLE 34

EFFECT OF VARIOUS CURING SYSTEMS ON 'THIOKOL' LP-2

Compound No.	34307-1	25999-6	38654-2	38651-3	38652-3	38653-4	38655-1	38656-6	38658-2	38656-3	38656-1
	Control										
LP-2 (Lot 387)	100	100	100	100	100	100	100	100	100	100	100
Zinc sulfide (ZS-800)	50	50	50	50	50	50	50	50	50	50	50
Lead stearate	1.4	--	--	--	--	--	--	--	--	1.4	--
Lead peroxide	7.5	--	--	--	--	--	--	--	--	7.5	--
Sulfur	--	--	--	--	0.25	--	--	0.25	0.25	0.25	--
Potassium dichromate	--	--	--	27	7	--	--	--	--	--	--
Triethanolamine	--	3	3	3	3	3	6	3	6	--	--
p-Quinonedioxime	--	--	3	--	--	3	3	3	3	--	--
Zinc chromate	--	7	7	--	--	--	--	--	--	--	--
Maleic anhydride	--	--	--	--	--	--	--	--	--	1	--
Cumene hydroperoxide (70%)	--	--	--	--	--	--	--	--	--	--	6
Triphenylguanidine (20%)	--	--	--	--	--	--	--	--	--	--	2
			Vulcanizate Properties (Cured 24 hr. @ 77°F)								
Shore hardness[a]	45	45	28	50	30	37	23	45	43	50	38

a Determined 48 hours after start of cure.

TABLE 35

EFFECT OF CURING AGENTS ON THE RESISTANCE OF 'THIOKOL' LP-2 COMPOUNDS TO HEAT AGING AT 212°F

Compound No.	34307-1	38656-3	38656-6
	Control Compound		
LP-2 (Lot 387)	100	100	100
Zinc sulfide (ZS-800)	50	50	50
Lead stearate	1.4	1.4	--
Lead peroxide	7.5	7.5	--
Triethanolamine	--	--	3
p-Quinonedioxime	--	--	3
Sulfur	--	0.25	0.25
Maleic anhydride	--	1.0	--
	Vulcanizate Properties (Cured 24 hr. @ 77°F)		
	a/b	a/b	a/b
Shore hardness	48/53	47/52	43/53
100% Modulus, lb/sq in.	160/150	175/175	138/160
300% Modulus, lb/sq in.	360/325	375/425	--/--
Tensile strength, lb/in.	440/340	360/500	280/350
Elongation, %	400/325	280/390	240/230
Weight/volume loss after aging at 212°F, %			
24 hr.	6/5	3/3	3/3
48 hr.	10/9	4/3	4/3
72 hr.	13/11	5/4	4/4
168 hr.	22/19	10/8	4/4
216 hr.	25[c]/22	12[c]/10	4[c]/3

a Unaged.
b Aged for 72 hours at 212°F.
c Specimens did not crack when flexed 180°.

FIGURE 11

DECREASE IN WEIGHT OF VARIOUS POLYMERS DURING HEAT AGING AT 212°F

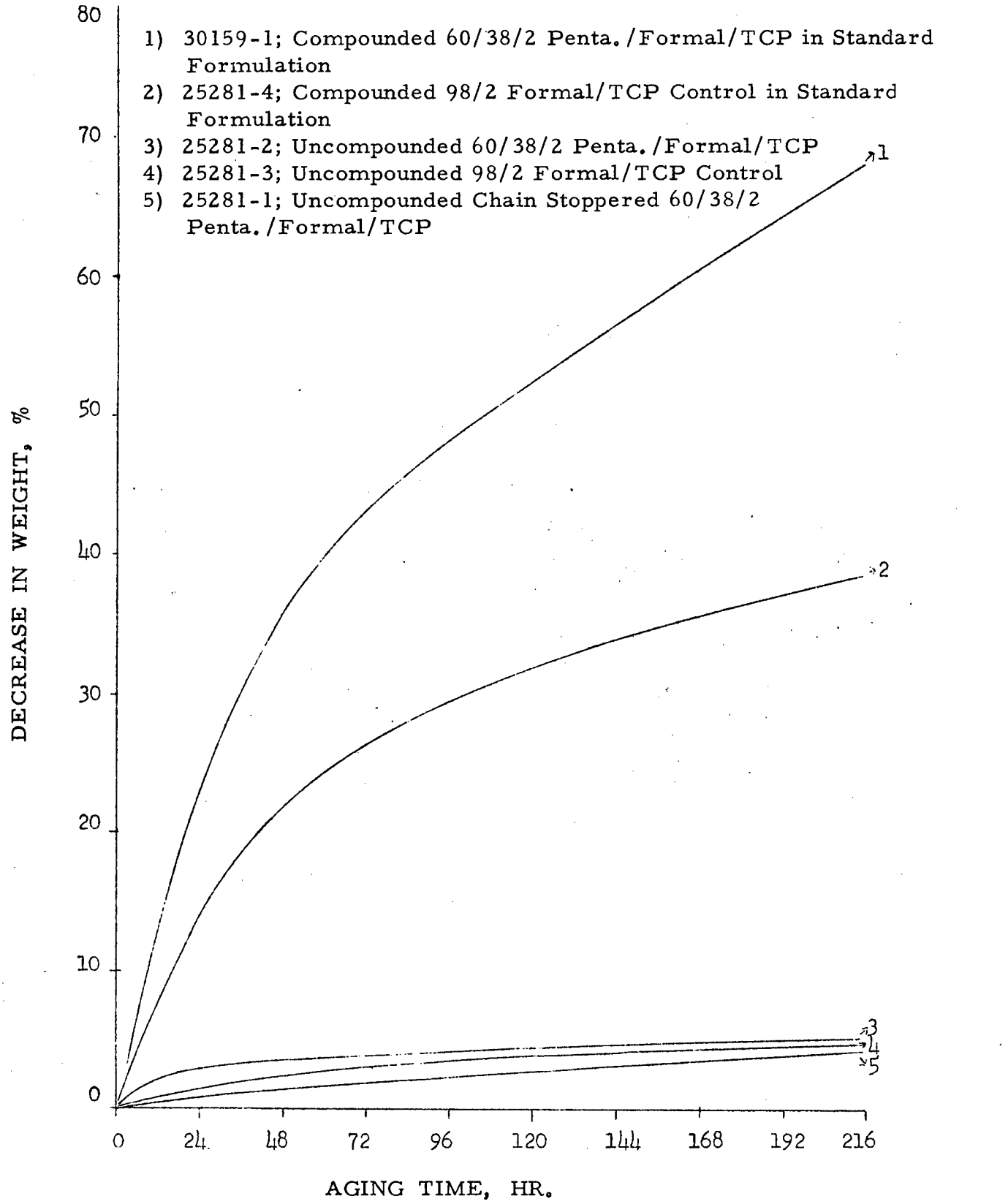


FIGURE 12

DECREASE IN WEIGHT OF VARIOUS 'THIOKOL' COMPOUNDS DURING HEAT AGING AT 212°F

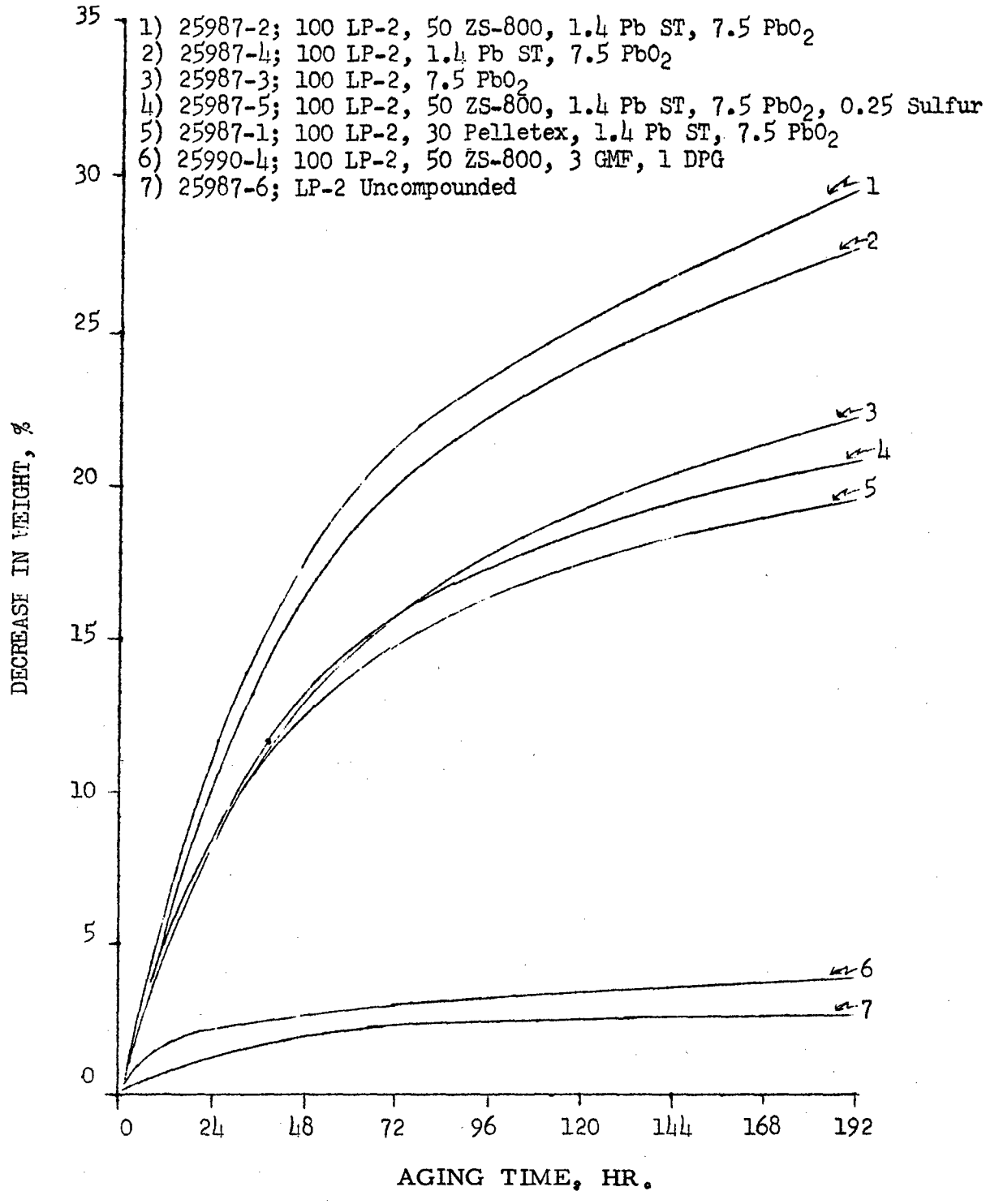


FIGURE 13

EFFECT OF FILLERS AND CURING AGENTS ON DECREASE IN WEIGHT OF 'THIOKOL' LP-2 COMPOUNDS DURING HEAT AGING AT 212°F

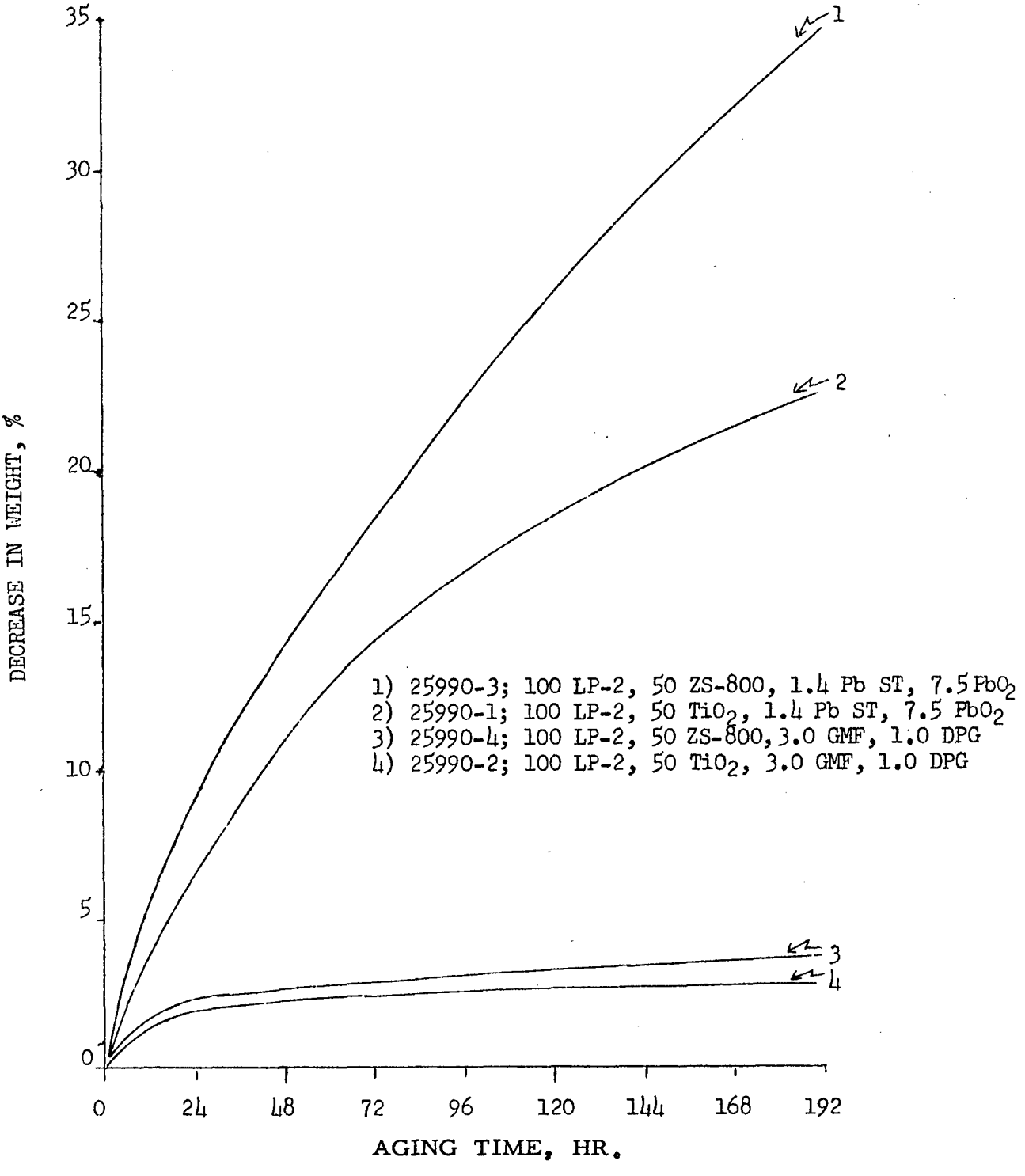


FIGURE 14

EFFECT OF AMOUNT OF LEAD PEROXIDE AND VISCOSITY ON THE WEIGHT LOSS OF 'THIOKOL' LIQUID POLYMER DURING HEAT AGING AT 212°F

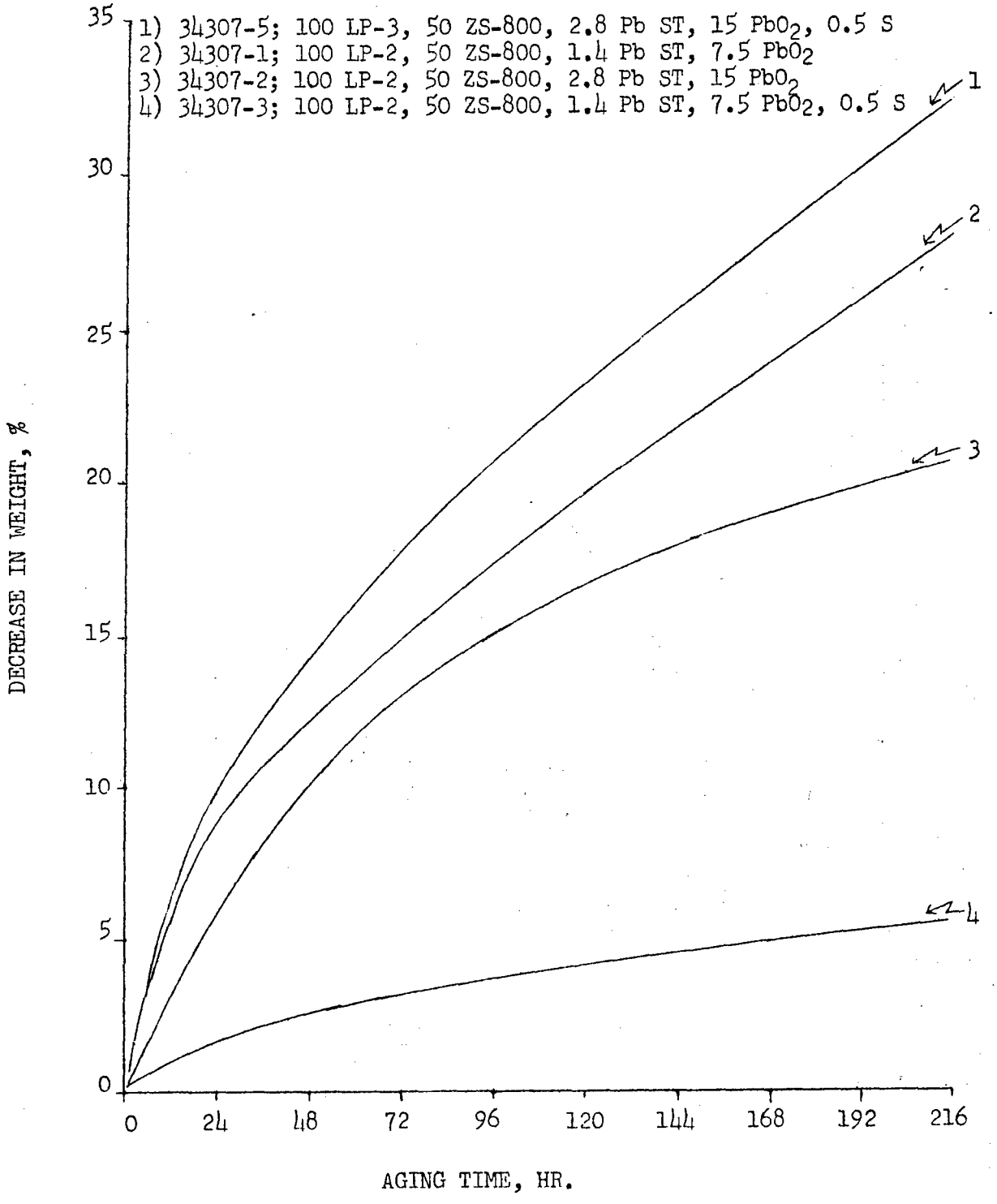
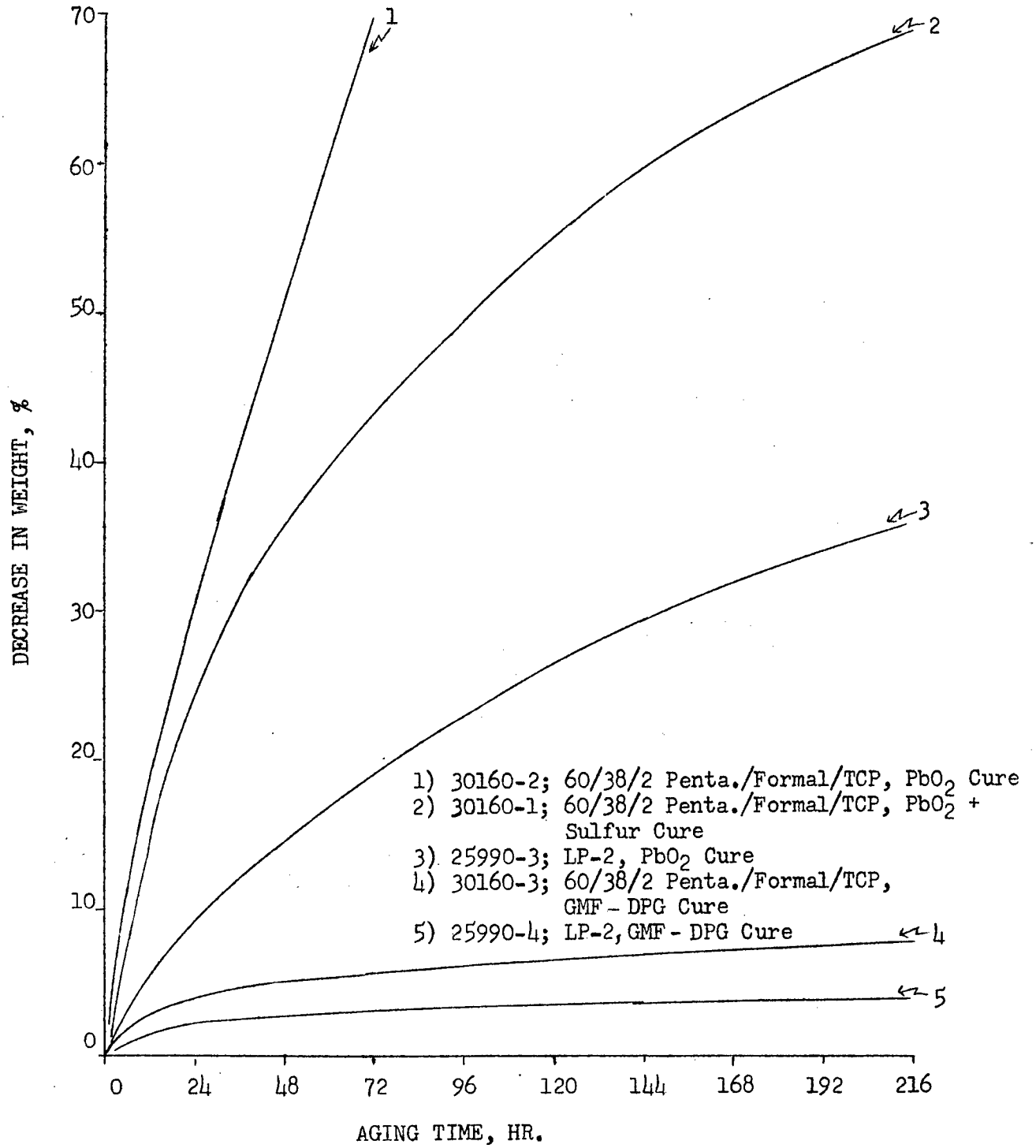


FIGURE 15

EFFECT OF CURING AGENTS ON DECREASE IN WEIGHT OF 'THIOKOL' LP-2 AND PENTAMETHYLENE/FORMAL COPOLYMER COMPOUNDS DURING HEAT AGING AT 212°F



III. DEVELOPMENT OF CLEAR SEALANT COMPOUNDS

As an approach toward the development of a clear sealant compound that would lead to a better sealing job during application of the sealant and would permit the detection of leaks in the fuel cell during service, various combinations of LP-2 and of LP-33 liquid polymers with a modified phenolic resin containing epoxide type polymer, BRR-18794, were investigated. Aromatic amines were employed in an attempt to obtain room temperature cures with these compounds. The data in Table 36 show that the working life (set time) of all but one compound was satisfactory, but that good cures were not obtained within 50 hours. Also, the materials obtained were generally tacky, weak, and 'short.' A more comprehensive evaluation of polymer BRR-18794 in combination with 'Thiokol' liquid polymers is shown in Table 37. In these tests, 0.075 x 6 x 6-inch test sheets were cast and cured to constant hardness at room temperature. All of the compounds tested had a low ultimate elongation. With the exception of the compound containing a 'Thiokol'/BRR-18794 polymer ratio of 3/1 (No. 30181-1), the highest ratio of liquid polymer to epoxide polymer, their tensile strengths were greater than 1000 lb/sq in. When the ratio of liquid polymer to BRR-18794 polymer was increased from 2/1 to 3/1, the tensile and tear strengths decreased and the elongation increased slightly (compounds No. 30175-1 and 30181-1). A non-crosslinked formal polymer of the same rank and approximately the same molecular weight as LP-2 was formulated with the BRR-18794 polymer in a 2 to 1 ratio (compound No. 30185-1). This compound possessed physical properties that were not significantly different than those of the crosslinked liquid formal polymer compounded in the same formulation.

A study was made with ZL-109 and combinations of LP-33 and ZL-158 and epoxide polymer RN-45, RN-48 and BRR-18794 polymer with dimethyl aminomethyl phenol as the curing agent in an effort to produce a more satisfactory material that would be suitable for a clear sealant compound. From the data in Table 38, it is apparent that all of the combinations evaluated possessed relatively long working life but did not cure within 24 hours at room temperature. Two combinations, compounds No. 28119-1 and 28119-2 cured to Shore hardness values of 55 and 75, respectively, after approximately 72 hours at room temperature. A visual and manual examination of these materials indicated that these compositions were quite tough.

Cure and adhesion studies were made with epoxide type polymers Pylene PC-2 and PC-10. These polymers were evaluated by themselves and in the LP-2 control formulation. They were also evaluated in a composition consisting only of 100 parts of LP-2, 10 parts of the epoxide polymer and its catalyst for possible use as a clear sealant compound. The data in Table 39 show that both epoxide polymers by themselves had sufficiently long set times, cured within 24 hours at room temperature, and possessed excellent adhesion to aluminum at room temperature. Cures were not obtained for the formulations containing only LP-2, the epoxide polymers and their catalysts. In the standard evaluation recipe extremely fast cures were obtained and the formulation with Pylene PC-10 had good adhesion to aluminum.

From the results obtained with the epoxide-liquid polymer compositions it is apparent that the most promising clear sealant compounds which have been

prepared thus far possess the following characteristics:

1. 'Short' ultimate elongation.
2. Good tear strength.
3. Poor compression set resistance at low temperature.
4. Good tensile strength.
5. Poor low temperature torsional stiffness properties.
6. Poor resistance to heat aging.
7. Good resistance to JP-3A jet fuel.
8. High hardness.

At first glance, the foregoing results with the epoxide polymers are not very promising. However, it should be pointed out that many of the defects in the compounds prepared appear to stem from too high a degree of crosslinking. Presumably, the use of an epoxide polymer of lower functionality with a low or noncrosslinked liquid polysulfide polymer will yield better compounds.

TABLE 36

CURE STUDIES OF 'THIOKOL' LIQUID POLYMERS WITH EPOXIDE TYPE POLYMER

Compound No.	28116-1	28116-5	28116-2	28116-6	28116-3	28116-7	28116-4
LP-2	100	--	100	--	100	--	100
LP-33	--	100	--	100	--	100	--
BRR-18794	10	10	20	20	30	30	40
DMP-10	1	1	1	1	1	1	4
Set time, hr.	8	Did not set in 50 hr.	6.5	6.75	6.5	4	6.5
Shore hardness at approx. 50 hr.	25	--	--	5	10	25	80
Remarks[a]	Quite tacky and 'short'	--	Tacky and 'short'	Soft, tacky, and weak	Soft, tacky, weak and crumbly	Tacky and 'short'	Very 'short' and brittle

a After visual and manual examination after 50-hour cure at room temperature.

TABLE 37

PROPERTIES OF CLEAR COMPOUNDS PREPARED FROM 'THIOKOL' LIQUID POLYMERS AND EPOXIDES

Compound No.	30175-1	30185-1	30181-1	30177-2	30177-3
50/50 ZL-158/LP-33	100	--	100	100	--
ZL-152	--	100	--	--	--
ZL-109	--	--	--	--	100
BRR 18794	50	50	33.3	100	100
Tri(dimethyl aminomethyl)phenol	5	5	3.33	--	--
Dimethyl aminomethyl phenol	--	--	--	7.5	7.5
Vulcanizate Properties (Cured to Constant Hardness @ 77°F)[a]					
	b/c	b	b/c	b	b
Shore hardness	93/67	95	89/60	94[d]	93
Tensile strength, lb/sq in.	1140/160	1300	700/150	1475	1050
Elongation, %	50/25	30	80/40	10	50
Tear strength, lb/in.	95/0	109	37/0	186	32
Compression set, %					
At 1 hour					
158°F	90	68	82	--	--
-40°F	82	87	82	--	--
Torsional test					
Relative modulus					
T_5, -°F	20	e	--	e	e
Absolute modulus					
G_{rt}, lb/sq in.	2570	--	--	--	--
$G_{5,000}$, °F	37	--	--	--	--
$G_{10,000}$	4	--	--	--	--
Decrease in weight, %	10[f]	7	14[f]	--	--
Decrease in volume, %	6	4	10	--	--
Swelling volume (1 month), %					
SR-6	6	--	10	--	--
SR-10	-1	--	2	--	--
JP-3A	5	--	2	--	--
Adhesion (cured to constant hardness)	Poor	--	--	Poor	Poor

a Unless indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Test sheets were brittle.
e Too stiff and 'short' for torsional test.
f Cracked when flexed 180°.

TABLE 38

CURE STUDIES OF 'THIOKOL' LIQUID POLYMERS WITH EPOXIDE TYPE POLYMERS FOR CLEAR SEALANTS

Compound No.	28119-7	28119-1	28119-2	28119-3	28119-4	28119-5	28116-8
ZL-109	--	100	--	--	--	--	--
ZL-158	--	--	50	50	50	50	--
LP-33	--	--	50	50	50	50	100
BRR 18794	100	100	100	50	--	--	30
Epoxide polymer RN-45	--	--	--	--	100	--	--
Epoxide polymer RN-48	--	--	--	--	--	100	--
Dimethyl aminomethyl phenol	10	7.5	7.5	3.75	7.5	7.5	2
Zinc sulfide (ZS-800)	--	--	--	--	--	--	50
Lead peroxide	--	--	--	--	--	--	12
Set time, hr.	4.75	8	9.5	9.75	9.5	6.5	7.0
Shore hardness							
At approx. 24 hr.	80	0	0	0	0	0	0
At approx. 72 hr.	80	55	75	5	55	35	5
Remarks[a]	Hard brittle	Fairly tough	Quite tough	Very tacky	-- Cold flow tacky		Cold flow tacky

a Visual and manual examination after 72 hours cure at room temperature.

TABLE 39

CURE AND ADHESION STUDIES WITH 'THIOKOL' LP-2 AND EPOXIDE TYPE POLYMERS

Compound No.	28134-1	28134-2	28134-3	28134-4	28134-5	28134-6
LP-2	--	--	100	100	100	100
Zinc sulfide (ZS-800)	--	--	--	--	50	50
Lead stearate	--	--	--	--	1.4	1.4
Lead peroxide	--	--	--	--	7.5	7.5
Pylene PC-2	14	--	10	--	10	--
Pylene PC-10	--	14	--	10	--	10
Catalyst for PC-2	1	--	0.72	--	0.72	--
Catalyst for PC-10	--	1	--	0.72	--	0.72
Set time[a]	Overnight	2 hr.	Not set after 48 hr.	Not set after 48 hr.	Set up on mill	5 min.
Shore hardness						
At 15 hr.	45	45	--	--	--	30
At 24 hr.	70	45	--	--	--	35
At 48 hr.	70	45	--	--	--	35
Adhesion[b]						
At 4 hr.	Excellent	Excellent	--	--	--	--
At 15 hr.	"	"	--	--	--	--
At 24 hr.	"	"	--	--	--	Good
At 48 hr.	"	"	--	--	--	"

a At room temperature.

b Compound spread on aluminum panel cleaned with VM and P Naphtha and evaluated for adhesion after each cure time interval by scraping with a knife.

IV. PROPERTIES OF POLYMERS MOST SUITABLE FOR SEALANT COMPOUNDS

A. INTRODUCTION

Experimental integral fuel cell sealant compounds were prepared from 60/38/2 mole % pentamethylene dichloride/formal/trichloropropane copolymer and 50/25/23/2 mole % hexamethylene dichloride/triglycol dichloride/formal/trichloropropane terpolymer. Both of these liquid polymers showed considerable promise in our screening evaluation tests for integral fuel cell sealant materials with improved low temperature properties; the terpolymer also displayed excellent resistance to heat aging at 212°F. However, the available quantities of these experimental polymers did not permit comprehensive compounding studies to be conducted for the development of sealant compounds. In addition to the two experimental polymer sealant compounds, a 'Thiokol' LP-2 sealant compound and a commercial LP-2 base sealant were also subjected to the standard screening tests and most of the requirement tests in Military Specification, Mil-S-5043A(Aer), for 'Sealing Compound'.

Samples of the three experimental sealant compounds ('Thiokol' LP-2, the copolymer and the terpolymer) were forwarded to Materials Lab, WADC Wright-Patterson Air Force Base.

B. EVALUATION OF COMPOUNDS

A comparison of the physical properties in Table 40 shows that the pentamethylene/formal copolymer and the hexamethylene/triglycol/formal terpolymer experimental sealant compounds were in the same category as the 'Thiokol' LP-2 compound. The copolymer compound appeared to be slightly inferior to the LP-2 material in ultimate elongation and the terpolymer sealant was somewhat poorer in tear strength. The physical properties of the samples aged for 72 hours at 212°F indicated that the experimental polymer compounds were as resistant to heat aging at 212°F as the LP-2 sealant material.

The pentamethylene/formal copolymer compound possessed better resistance to compression set at 158°F than the terpolymer and the LP-2 sealant materials. At 158°F, the terpolymer compound was comparable to the LP-2 sealant in resistance to compression set, but at -40°F, the resistance to compression set was poor; this value is not in conformance with the result obtained with this terpolymer in the standard evaluation formulation.

Both of the experimental polymer sealant compounds possessed improved low temperature properties over the LP-2 compound. This is evident from the relative and absolute moduli data recorded in Table 41 and is graphically illustrated by the curves in Figures 16 and 17. In this respect, the terpolymer was outstanding; it gave a 5,000 lb/sq in. absolute torsional modulus at -85°F, whereas the LP-2 compound attained this modulus at -61°F. The tension-retraction data (TR values) also show the superiority of the two experimental polymer sealant compounds in this property at low temperatures. The pentamethylene/formal compound started to retract at -85°F, the terpolymer sealant material at -95°F

and the 'Thiokol' LP-2 compound at -75°F (see Figures 18 and 19). The copolymer sealant material attained 10, 30, 50 and 70% retraction at temperatures approximately 12°F lower than the LP-2 material and the terpolymer compound reached 10, 30 and 50% retraction at even lower temperatures. However, at 65% retraction (-40°F), the terpolymer sealant did not retract any more until a temperature of 55°F was reached. These data were checked on the same specimen on the following day with the same results. This peculiarity in the tension-retraction characteristics was not obtained with this terpolymer in our standard evaluation formulation. This phenomenon will be investigated further when more hexamethylene/triglycol/formal terpolymer is available.

Aging tests conducted at 212°F showed that the copolymer sealant compound was somewhat better than the LP-2 sealant material with respect to decrease in weight and volume and increase in hardness during heat aging. This test could not be conducted on the terpolymer sealant compound because of the small quantity available.

The working life of the two experimental polymer and LP-2 sealant compounds varied from 2 to 2.5 hours. A longer working life would be desirable and should be attainable by making minor changes in the compound or curing agent. The use of the epoxide polymer in the compounds increased the viscosity of the compounds and decreased working life.

The volume change of the copolymer sealant in Type III fuel (similar to SR-6) was 2.5 times that of the LP-2 sealant (See Table 41 for test data). Also, it was observed in the adhesion tests conducted on the specimens immersed in the Type III fuel that the two experimental polymer sealant compounds were somewhat weaker than the LP-2 compound. In Type I fuel (similar to SR-10) the volume change of the copolymer sealant compound was comparable to that of the LP-2 sealant material.

The adhesive bond strength of the three experimental sealant compounds to aluminum could not be quantitatively determined as the fabric pulled away from the rubber before adhesion failure occurred. However, the specific adhesion of the three compounds to aluminum appeared to be very good. The adhesion properties of the compounds after long term aging were not determined.

According to the results in Table 41, the two experimental polymer and LP-2 sealant compounds met the requirements of the Military Specification, Mil-S-5043 (Aer) tests to which they were subjected with the possible exception of adhesion to aluminum.

TABLE 40

PROPERTIES OF EXPERIMENTAL INTEGRAL FUEL CELL SEALANT COMPOUNDS

	LP-2 Sealant	LP-2 Base Commercial Sealant	Penta/Formal Sealant (Poly. No. A46113B1)	Hexa/Triglycol/ Formal Sealant (Poly. No. 20199E)
		Polymer Properties		
Formal, mole %	98	--	38	23
Pentamethylene dichloride, mole %	--	--	60	--
Hexamethylene dichloride, mole %	--	--	--	50
Triglycol dichloride, mole %	--	--	--	25
Trichloropropane, mole %	2	--	2	2
Brookfield viscosity, poises	460	--	260	285
		Formulations		
Compound No.	34385-5	34385-4	34385-2	34385-3
LP-2 (Lot No. 387)	100	--	--	--
Commercial sealant compound	--	100	--	--
Penta/formal	--	--	100	--
Hexa/triglycol/formal	--	--	--	100
Pelletex SRF-3	30	--	30	30
Maleic anhydride	1	--	2	2
Epoxide polymer C-8	0.5	--	0.5	0.5
Lead peroxide paste C11 (parts/100 parts of base compound)	9.6	--	9.4	9.4
Commercial sealant compound Curing Agent	--	12	--	--
	Processing Data (cured 24 hr. @ 80°F, 50-55% R.H.)			
Working Life, hr.	2 (approx.)	3 (approx.)	2.5	2 (approx.)
Press out Time, min.	10	10	10	10
Press out Temp., °F	300	300	300	300

(Table continued on next page.)

TABLE 40 (Contd.)

	LP-2 Sealant	LP-2 Base Commercial Sealant	Penta/Formal Sealant (Poly. No. A46113B1)	Hexa/Triglycol/ Formal Sealant (Poly. No. 20199E)
		Screening Test Data for Cured Compounds[a]		
	b/c	b/c	b/c	b/c
Shore hardness	53/60	58/69	58/60	54/60
100% Modulus, lb/sq in.	175/260	200/512	275/325	225/250
300% Modulus, lb/sq in.	550/840	---	---	600/800
Tensile strength, lb/sq in.	700/860	425/600	725/915	600/800
Elongation, %	380/310	220/130	260/265	300/300
Tear strength, lb/in.	57/92	30/35	54/70	33/70
Compression Set, % at 1 hour				
158°F	65	98	50	64
-40°F	29	57	31	90
Torsional Test				
Relative modulus				
T_5, -°F	49/47	45/50	59/61	77/77
T_{10}	55/53	52/56	66/68	81/82
T_{50}	64/64	62/65	76/77	88/89
T_{100}	66/66	64/67	77/80	90/91
Absolute modulus				
G_{rt}, lb/sq in.	167/252	188/426	178/286	180/290
$G_{5,000}$, -°F	61/59	59/58	73/72	85/84
$G_{10,000}$	64/63	62/61	76/75	88/87
$G_{20,000}$	65/66	65/64	78/79	90/90

(Table continued and footnotes on next page.)

TABLE 40 (Contd.)

	LP-2 Sealant	LP-2 Base Commercial Sealant	Penta/Formal Sealant (Poly No. A46113B1)	Hexa/Triglycol/ Formal Sealant (Poly No. 20199E)
	Screening Test Data for Cured Compounds			
Tension-Retraction				
TR 10, -°F	63	60	75	85
TR 30	56	50	68	75
TR 50	48	36	59	63
TR 70	34	18	44	+55
TR 10-TR 70	29	42	31	--
Decrease in Weight, %	7[c]	8[c]	4[c]	--
Decrease in Volume, %	7[c]	9[c]	5[c]	--
Increase in Hardness, %	13[c]	19[c]	4[c]	--
Swelling Volume, %				
JP-3A 1 Day	2	2	4	--
1 Week	4[d]	6[d]	10	--

a Unless indicated otherwise, the specimens were unaged.
b Unaged.
c Aged for 72 hours at 212°F.
d Surface of specimen attacked.

TABLE 41

RESULTS OF MILITARY SPECIFICATION, MIL-S-5043(Aer), TESTS

	Specification Limits	LP-2 Sealant	LP-2 Base Commercial Sealant	Penta/Formal Sealant	Hexa/Triglycol/ Formal Sealant
Non-volatile content total solids, %	98 min.	99 (passed)[a]	98 (passed)	99 (passed)	--
Adhesion, lb/in.					
After 24-hr. cure	--	17[b]	27[c]	10[b]	12[b]
After 48-hr. in type III fuel	10 min.	8[b]	30[d]	5[b]	4[b]
Resistance to heat	--	OK (passed)	Some increase in hardness	OK (passed)	OK (passed)
Resistance to salt water and hydrocarbons	--	Lost Adhesion	Some increase in hardness in Type III fuel	OK (passed)	OK (passed)
Low temperature flexibility	-70°F min.	OK (passed)	OK (passed)	OK (passed)	OK (passed)
Volume change, %					
After 24 hr. in Type III fuel	+20 max.	5 (passed)	7 (passed)	12 (passed)	--
Dried at 80°F for 48 hrs.	-5 max.	1 "	1 "	0.5 "	--
After 24 hrs. in Type I fuel	+20 max.	1 "	0.5 "	0.5 "	--
Test fluid contamination					
Non-volatile extractible material, mg./100ml.	60 max.	32 "	28 "	36 "	--
Discoloration	--	Very slight discoloration (passed)	Very slight discoloration (passed)	None (passed)	--
					--

a Passed specification requirements.
b Fabric pulled away from rubber. Good adhesion to aluminum test panel.
c Failure at bond between rubber and aluminum test panel and cohesive failure of rubber.
d Cohesive strength failure of rubber.

FIGURE 16

RELATIVE TORSIONAL MODULUS VERSUS TEMPERATURE FOR EXPERIMENTAL SEALANTS

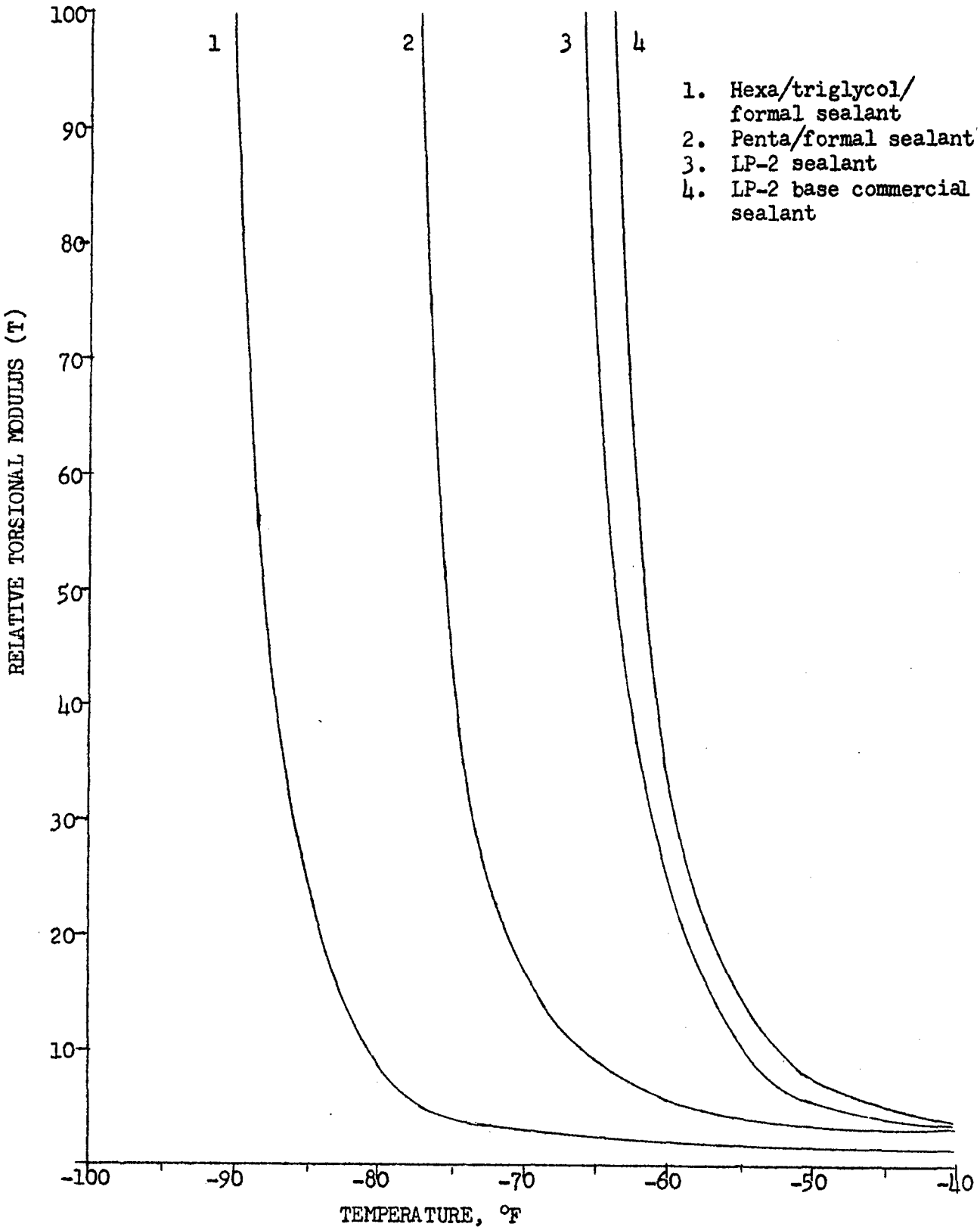


FIGURE 17

ABSOLUTE TORSIONAL MODULUS VERSUS TEMPERATURE FOR EXPERIMENTAL SEALANTS

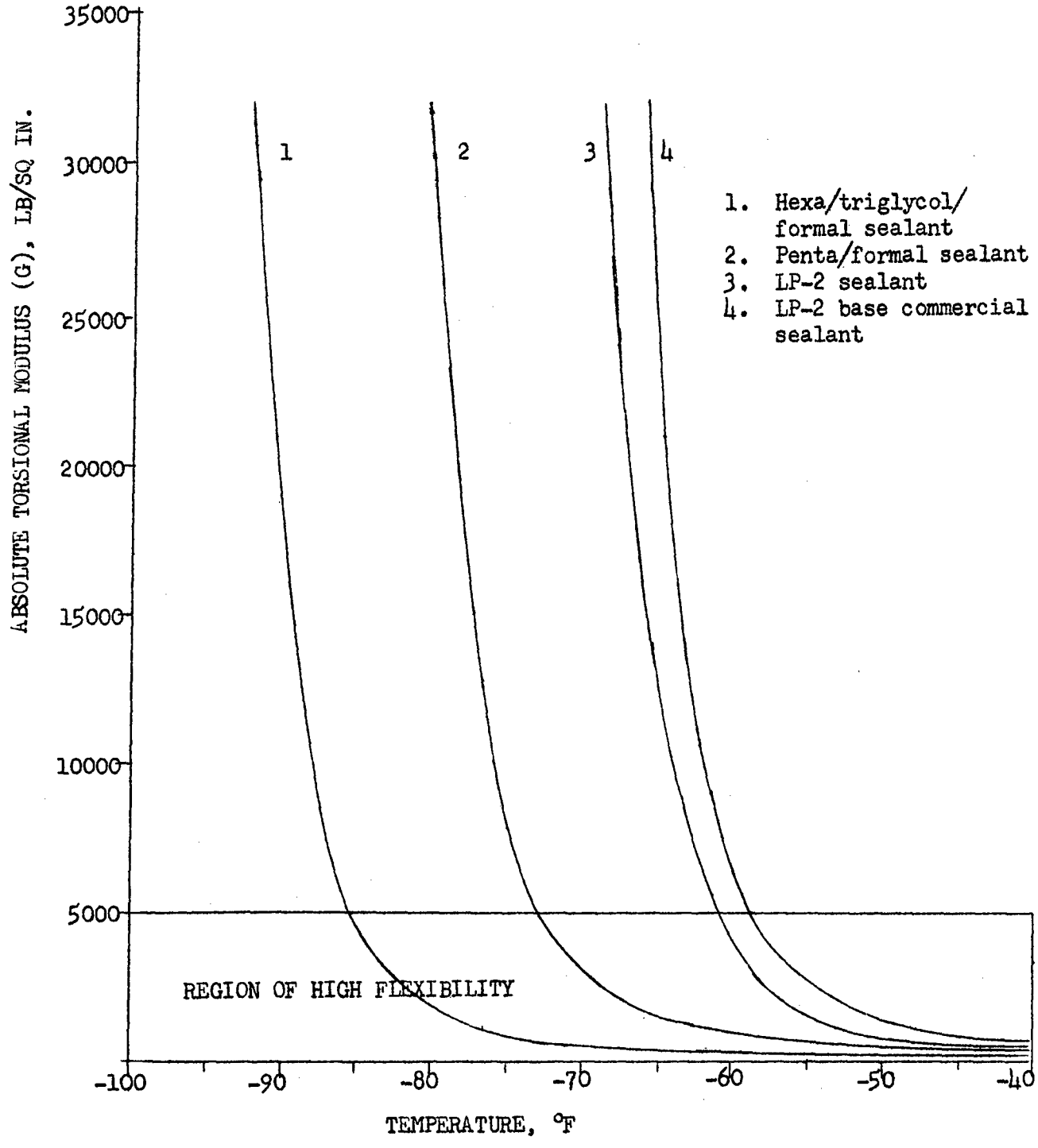


FIGURE 18

TENSION-RETRACTION VERSUS TEMPERATURE FOR EXPERIMENTAL SEALANTS

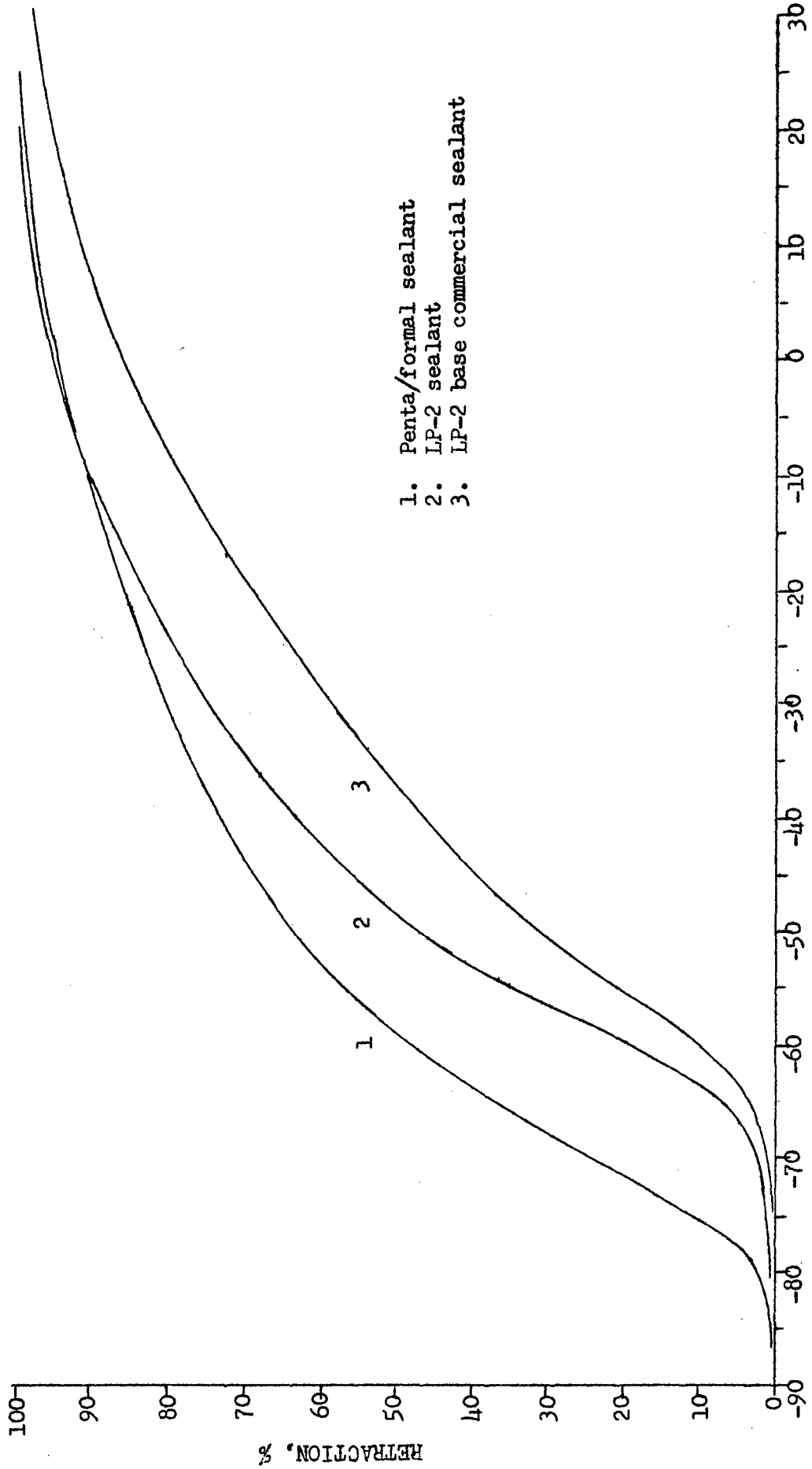
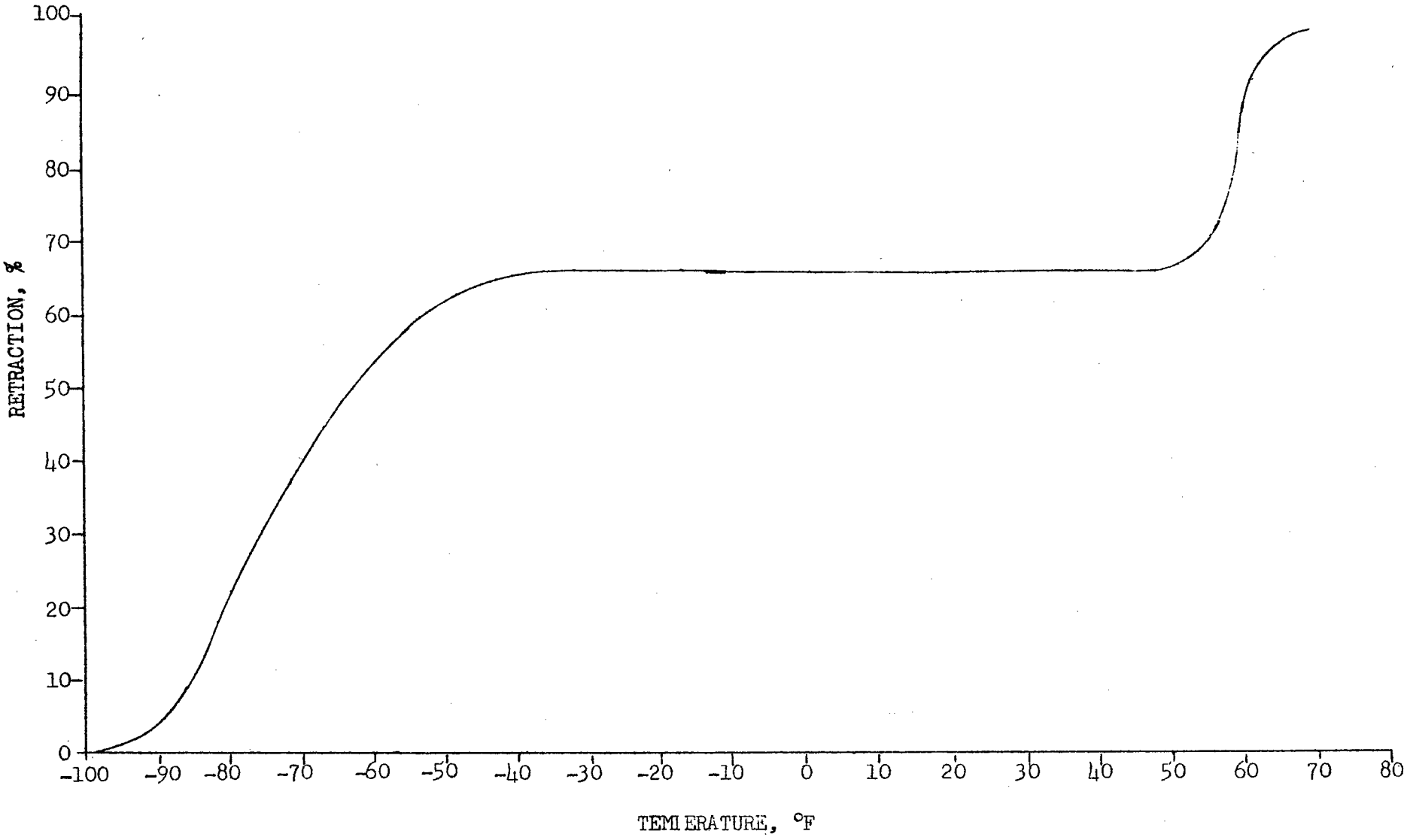


FIGURE 19

TENSION-RETRACTION VERSUS TEMPERATURE OF
HEXA./TRIGLYCOL/FORMAL SEALANT COMPOUND



APPENDIX A

POLYMER PREPARATION PROCEDURES

I. STANDARD REACTION PROCEDURE FOR POLYMER PREPARATION

Reaction

$$ClRCl + Na_2S_x \longrightarrow (-RS_x-)_n + 2NaCl$$

Apparatus

5-Liter, 3-neck round bottom flask fitted with stirrer, reflux condenser, dropping funnel and thermometer.

Procedure

Place 4.8 moles of sodium polysulfide solution of the required rank (about 2 molar concentration) in the flask. Heat with a Bunsen burner and stir. Add, while stirring and heating, 20 ml. of 5% Nekal BX solution and 17 ml. of 50% sodium hydroxide. Then add 117 ml. of 25% magnesium chloride hexahydrate dropwise from the addition funnel.

Continue heating until the temperature of the reaction mixture reaches 200°F. At this point, remove the burner and start adding slowly 4 moles of halide (mixed in the proper molar ratio to give the desired copolymer). The rate of addition should be such that the entire amount will be added over the course of one hour. Temperature of the reaction is controlled partly by the rate of halide addition. If the temperature rises above 200°F, cool the flask by playing a stream of cold water against it.

After the halide has been added, heat the reaction mixture to 212°F and continue heating for one hour. At the end of this time, dilute the reaction mixture with cold water and fill the flask. Continue agitation for a minute or two then stop the stirrer. When the latex has settled, siphon off the supernatant liquid and stir and dilute again, this time with hot water. If the latex is not to be toughened, continue washing in this manner until the supernatant liquid shows no discoloration of lead acetate test paper.

If the latex is to be toughened, stir and heat the latex after removal of the second wash liquid. When the temperature reaches 210°F, add 1 mole of sodium polysulfide (rank 2.25), and maintain the temperature at 200°F for 30 minutes. At the end of this time, dilute the reaction mixture with cold water and wash the latex clean as described above.

When the latex is free of sulfide, remove as much of the supernatant liquid as possible, transfer the latex to a jar and determine the total solids.

Variations

Reactions as large as 5 moles and as small as 2 moles may be conducted in 5-liter flasks. Reactions of one mole and smaller are run in 1-liter, 3-neck flasks. The halides are added over a shorter period of time for the smaller reactions.

Washing time may be greatly shortened by transferring the latex to a large battery jar and using large volumes of wash water.

Possible variations include using dispersing agents other than Nekal BX and condensation nuclei other than magnesium hydroxide.

In cases where the halide is too volatile to permit reaction at 200°F, the halide is added at a temperature that will just cause gentle refluxing. The temperature is raised to 212°F at the end of the halide addition, as stated previously.

If steam distillation is necessary to remove volatile side-reaction products, it is generally done after the latex has been washed twice, although it may be done at any time after the reaction is complete.

II. LIQUID POLYMER PREPARATION

The polymers and copolymers are converted to liquid polymers and copolymers with thiol terminals by reducing some of the disulfide units in the latex to thiols with sodium sulfhydrate and sodium sulfite. The following equation represents the over-all reaction, although it does not indicate the mechanism:

$$RSSR + NaHS + Na_2SO_3 \longrightarrow RSH + NaS\text{-}R\text{-} + Na_2S_2O_3$$

The NaS - R - is converted to H-S-R upon acidification.

Procedure

Put the required amount of latex with a total solids of approximately 30% in a beaker. Heat to 180°F with continuous stirring. When this temperature is reached, add sodium sulfhydrate and sodium sulfite (1.1 moles/mole of latex). The amount of sulfhydrate to use is estimated from the durometer reading on a dried filter cake of the latex and from consideration of the inherent properties of the polymer.

After the splitting salts have been added, continue heating at 180°F for 30 minutes. At the end of this time, dilute the latex with cold tap water. Wash the split latex by decantation with hot water until a one-mole sample of the supernatant liquor fails to decolorize a few drops of dilute (light amber color) iodine-potassium iodide solution.

Decant the mixture to half volume and adjust it to pH of 4 with a 50% solution of glacial acetic acid. Dilute with cold water and let the solids settle. Wash the mixture with hot water till a pH of 6 is reached. Pour off all the water and dry the split latex in the oven at 158°F.

III. PREPARATION OF COPOLYMERS BY REDISTRIBUTION

Calculate the amount of each latex needed to yield the desired copolymer. Mix the latices in a beaker and heat with stirring to 180°F. Add sodium polysulfide (rank 2-2.25), 0.1 mole per mole of copolymer and maintain the temperature at 180°F for one-half hour. Dilute the latex with cold tap water, allow it to settle and draw off the supernatant liquid. Continue washing in this manner with hot tap water or until the supernatant liquid shows no discoloration of lead acetate test paper. Draw off the final wash liquid, put the latex in a jar, and determine the total solids.

If it is desired to toughen the polymer during redistribution, use 0.25 mole of sodium polysulfide instead of 0.1 mole per mole of polymer.

IV. PREPARATION OF CRUDE RUBBER BY SPLITTING

Procedure

Put the required amount of latex in a beaker. Heat to 180°F with continuous stirring. When this temperature is reached, add sodium sulfhydrate and sodium sulfite, the latter 11 times the molar quantity of the former. The amount of sulfhydrate to use is estimated from the durometer reading on a dried filter cake of the latex, based on previous experience with the type of polymer being split.

After the splitting salts have been added, continue heating at 180°F for 30 minutes. At the end of this time, dilute the latex with cold tap water. Wash the latex by decantation with cold tap water until a 1 ml. sample (approx.) of the supernatant liquor fails to decolorize an approximately equal volume of dilute (light-amber colored) iodine-potassium iodide solution.

When the latex is sulfite-free, as shown by the iodine test, coagulate a small amount of latex by adding a soap (sodium stearate) dispersion and a little 50% acetic acid. If the trial coagulum appears too soft, it is sometimes advantageous to let the split latex stand overnight or longer before coagulating. If the trial coagulum seems to be much too tough, the splitting procedure may have to be repeated on all or part of the latex.

Coagulate the split latex by adding a water dispersion of soap (sodium stearate) containing an amount of soap equal to 1% of the polymer weight and by adding slowly, with stirring, sufficient 50% acetic acid to bring the pH to 4.0. Wash the coagulum two or three times by decantation with hot water to remove the acetic acid. The soap dispersion can be prepared by making a stiff paste of the finely powdered soap in cold water and diluting it rapidly with boiling water. If the

coagulum does not form a clump, allow it to settle. In some cases it may be necessary to collect the coagulum on a screen or filter.

Squeeze the coagulum as dry as possible by hand, and mill it on a warm rubber mill until it is dry. Remove from the mill as a sheet.

V. POLYMER STRIPPING PROCEDURES

Stripping with Caustic

While stirring the latex, heat it to 170°F. At this point sodium hydroxide (50% solution) is added, generally at the ratio of 1 mole of sodium hydroxide per mole (segment) of polymer. Maintain the temperature at 170°F for 1 hour. At the end of this time dilute the latex with cold water, allow it to settle, and decant the supernatant liquid. Follow with another wash in the same manner with hot water. A monosulfide strip can follow at this point, or the washing can be repeated until the latex is clean (free of sulfide by the lead acetate test).

Stripping with Caustic

This procedure generally follows a caustic strip. Heat the latex to 180°F, and add sodium monosulfide solution (about 2 molar), generally at the ratio of 0.1 mole per mole of polymer segment. Maintain the latex at 180°F for 30 minutes, then dilute with cold water and finally wash by decantation until it is sulfide-free.

Stripping with Sodium Sulfite

Heat the latex to 180°F. Add anhydrous sodium sulfite, 1 mole per mole of sulfur to be stripped and maintain the temperature at 180°F for 30 minutes. At the end of this time, dilute the latex with cold water, allow it to settle and decant. Repeat the washing until a few drops of clear supernatant liquor fails to decolorize about 0.5 ml. of iodine-potassium iodide solution (light-amber colored).

APPENDIX B

EVALUATION PROCEDURES

I. COMPOUNDING AND PROCESSING OF POLYMERS

Most of the experimental polymers were compounded according to the following standard evaluation recipe:

Ingredients	Parts
Experimental polymer	100
Zinc sulfide (ZS-800)	50
Lead stearate	1.4
Lead peroxide	7.5

The compounds were processed by giving them three passes on the paint mill. They were then cured at 77° to 80°F and a relative humidity of 55 to 60% for 24 hours. After curing, the stocks were sheeted on a cold two-roll mill and then molded at 287°F for 10 minutes.

In the additive studies, 10 parts of the additive per 100 parts of 'Thiokol' liquid polymer LP-2 were compounded in the foregoing formulation. The stocks were processed and cured in the same manner as described in the preceding paragraph.

II. EVALUATION METHODS

With the exception of the adhesion, compression set and viscosity determinations, the following tests were conducted on samples cut from 0.075 x 4 x 6-inch molded sheets.

1. Hardness and Stress-Strain Relationship at Room Temperature

Hardness was determined by means of the Shore A durometer at 77° to 80°F. All readings were taken after a 5-second time interval.

The stress-strain relationship, ultimate tensile strength, and elongation were obtained in accordance with the tentative method of test for 'Tension Testing of Vulcanized Rubber', ASTM Designation D412-49T.

2. Stress-Strain Relationship at Various Temperatures

Test specimens were cut from the molded sheet of the test compound with a type C die, A.S.T.M. Designation: D412-49T, and fastened in the clamps of the test jig attached to a Scott Tensile Testing Machine (see Figure 20) so that the distance between the clamps was 0.5 in. For temperatures below 80°F, a Dewar flask containing isopropyl alcohol at the test temperature was placed in position in the test jig which contained the test specimen. When necessary, the

temperature was maintained with dry ice and an electric strip heater. After conditioning for 3 minutes at the test temperature, the specimen was stressed at a jaw separation speed of 2 inches per minute; the stress-strain relationship was recorded on the 'Tensilgram' chart. Tests were conducted in duplicate at each temperature and the results were averaged. Curves showing the relationship between ultimate tensile strength, ultimate elongation and modulus of stretch at failure and temperature were plotted. The modulus of stretch at failure was calculated from the equation:

$$\text{Modulus of stretch at failure} - M_{SF} = \frac{\text{Ultimate Tensile Strength (lb/sq in.)} \times 100, \text{ lb/sq in.}}{\text{Ultimate Elongation (\%)}}$$

3. Compression Set

This property was determined on molded plugs at 180°, 150°, -20°, and -40°F in conformance with Method B, ASTM Designation D395-49T, except that the specimens were subjected to a compression of 25% and exposed to the test temperatures for one hour.

The jigs were conditioned for one hour at the test temperature before the samples were tested. Measurements were taken 30 minutes after removal of the specimens from the jig. In the elevated temperature tests, the plugs were cooled at room temperature after removal from the jigs, whereas the plugs tested at the low temperatures were maintained at the test temperature after removal from the jigs.

4. Torsional Stiffness at Low Temperatures

The low temperature behavior of the compounds was studied with the torsional tester, which is a modification of the tester specified in ASTM Designation D1043-49T for 'Stiffness Properties of Nonrigid Plastics as a Function of Temperature by Means of a Torsional Test'. The absolute shear modulus in pounds per square inch at various temperatures was calculated from the degree of twist of the sample. These data were then plotted and the temperatures at which the specimen gave absolute torsional modulus values of 5000, 10,000 and 20,000 lb/sq in. were read from the curve. To determine the relative stiffening of the samples, the torsional modulus obtained at each temperature was divided by that at 64°F. These data were also plotted and the temperatures at which the shear modulus at 64°F (G_{rt}) was increased five (T_5), ten (T_{10}), fifty (T_{50}) and one hundred (T_{100}) times was determined from the graph.

Since the absolute torsional modulus gives a measure of the actual stiffness of the sample rather than the comparative stiffness, emphasis was placed on the absolute values in evaluating the low temperature stiffness of the compounds.

5. Tension-Retraction

Basically, the tension-retraction test is an adaptation of the T-50 test for determining the 'Physical State of Cure of Vulcanized Rubber', ASTM Designation D599-40T. Two-inch T-5 specimens were stretched to 100% elongation on a rack and then immersed in an ethanol (Ponsolve) conditioning bath at -95°F for 10 minutes. The rack was then transferred to the test bath at -95°F and the tension on the specimens was released. After the bath was adjusted to a constant warm-up rate of 2°F per minute, readings were taken every 2.5 minutes as the samples retracted. Temperature versus percentage retraction was plotted and the temperature at which the specimens retracted 10 (TR10), 30 (TR30, 50 (TR50), and 70% (TR70) of the original elongation were determined from the graph. A large temperature differential between the TR10 and TR70 values indicates a low rate of retraction.

6. Solvent Resistance

This test was conducted according to ASTM Designation D471-49T, Method D, employing SR-6, SR-10 and JP-3A fuels. The samples were measured for length after one-day, one-week, two-weeks and one-month immersion periods. Percentage volume change was calculated from the increase or decrease in length of the sample.

7. Adhesion

The adhesion characteristics of some of the experimental polymers and LP-2 additives to 24 ST Alclad aluminum were evaluated according to qualification test procedure 4.3.2.3. in specification Mil-S-5043A (Aer). However this test was not very satisfactory for our use. Our experience has shown that when properly compounded with additives for imparting adhesion, the adhesive strength of the experimental copolymers to aluminum was higher than the cohesive strength and/or that of the cotton fabric. Also, this test requires too much polymer. Therefore, the test was replaced with a 'spot' test in which a small quantity of the experimental compound was spread in a layer approximately 0.125-inch thick on 24 ST Alclad aluminum test panel cleaned with VM & P naphtha. The adhesion properties were measured by visual observation and by scraping with a knife after the 24-hour cure at 77° to 80°F and 55 to 60% relative humidity and then after 48 hours of immersion in SR-6 fuel at 80°F. The polymers were rated for adhesion in comparison to the formal control as excellent, good and poor.

8. Viscosity

All liquid polymers were tested for viscosity before compounding. Measurements were made with the Brookfield viscometer after conditioning the samples for 3 hours at 80°F.

9. Change in Weight and Volume During Aging at 212°F

Test specimens 0.075 x 1.5 x 3 inches in size were cut from the molded

sheet of the test compound. The weight of the specimen was determined in air to 0.01 gram and the volume was measured by the loss of buoyancy of the sample in distilled water at room temperature after 0, 24.48, 72, 144, 168, and 216 hours of aging at 212°F. Aging tests were conducted in a Fisher forced draft oven. Percentage change in weight of the specimens was calculated on the basis of the polymer weight in the compound before heat aging.

10. Shear and Tension Test (Concentrated Stress) at Various Temperatures [1]

The sketches in Figure 21 illustrate the nature and size of the specimens used in this test. All specimens were cured in the sample preparation jig for 24 hours at 77 to 80°F before testing. The test specimens were fastened in the clamps of a test jig attached to a Scott Tensile Testing Machine. The equipment used in this test is shown in Figure 20. After conditioning for 3 minutes at the test temperature, the specimen was stressed at a jaw separation speed of 2 in/min. and the stress-strain relationship recorded on the 'Tensilgram' chart. Tests were conducted in duplicate at 180°, 80° and -65°F. Glycerin was used for the test bath at 180°F and isopropyl alcohol for the -65°F medium. The modulus of stretch at initial failure was calculated from the equation:

$$\text{Modulus of Stretch at Initial Failure} = \frac{P/L_1 \times 100}{E}, \text{ lb/in.}$$

P = Load in pounds at initial failure.
L_1 = Width of specimen in inches.
E = Percent elongation at initial failure.

Tests were started with an LP-2 base commercial sealant (Compound No. 25954-3) and the LP-2 control formulation containing 0.25 part each of maleic anhydride and furoic acid per 100 parts of LP-2.

According to the results in Tables 42 and 43, the commercial sealant compound possessed a somewhat lower elongation and required a higher load for initial failure of the specimen than the LP-2 control compound at -65°F. This resulted in a considerably higher modulus of stretch at initial failure for the commercial sealant than for the LP-2 control; that is, the commercial sealant was not as elastic at -65°F as the LP-2 control. At 80°F, the commercial sealant displayed slightly higher elongation, lower load and lower modulus of stretch at initial failure than the LP-2 control compound; however, the properties of the two compounds were generally in the same range. The commercial sealant compound was very thermoplastic at 180°F and it was not possible to cause the specimens to fail either in adhesion or cohesion. The LP-2 control formulation was comparatively 'short' and weak at 180°F but its modulus of stretch at initial failure was in the same range as that obtained at 80°F. With exception of one specimen, which was tested at -65°F, all of the LP-2 control compounds failed from lack of cohesive rather than adhesive strength. Thus, our adhesion additives provide good adhesion not only at 80°F, but also at elevated and low temperatures.

1 Douglas Aircraft Company, 'Integral Fuel Tank Sealants', Report No. RL-8403, 12 March 1946.

11. Military Specification, Mil-S-5043A(Aer), Requirement Tests Employed for Experimental Sealant Compounds in Section III.

a. Working and Curing Time, Test No. 3.3.4 and 3.3.5
b. Non-volatile Content, Test No. 4.3.2.1
c. Adhesion, Test No. 4.3.2.3
d. Resistance to Heat, Test No. 4.3.2.4
e. Resistance to Salt Water and Hydrocarbons, Test No. 4.3.2.5
f. Low Temperature Flexibility, Test No. 4.3.2.6
g. Test Fluid Contamination

(1) Non-volatile Extractable Material, Test No. 4.3.2.7.1

Because of limitations in the available test equipment the contaminated test fuel was evaporated at 150°C in lieu of 160° to 165°C as specified in the Air Jet Method of Specification VV-L-791.

(2) Discoloration, Test No. 4.3.2.7.3

h. Volume Change, Test No. 4.3.2.9

TABLE 42

SHEAR AND TENSION TEST DATA FOR COMMERCIAL SEALANT COMPOUND NO. 25954-3

Temp., °F	80		-65		180	
Specimen Size						
Thickness, in.	0.130	0.133	0.133	0.134	0.133	0.130
Width (L), in.	0.492	0.485	0.493	0.493	0.487	0.487
Gage length, in.	0.25	0.25	0.25	0.25	0.25	0.25
Area, sq/in.	0.064	0.064	0.066	0.066	0.065	0.063
Length @ failure, in.	1.15	1.30	0.55	0.55	3.75[a]	3.85[a]
Physical Properties						
Elongation for initial failure, %	360	420	120	120	1400[a]	1450[a]
Load (P) @ initial failure, lb.	9	10	172	174	3[b]	2.5[b]
Modulus of stretch @ initial failure						
$\frac{P/L_1 \times 100}{\%\ \text{Elong.}}$, lb/in.	5	5	290	294	---	---
Type of failure	Adhesive	Adhesive	Cohesive	Cohesive	---	---

a Specimen stretched to this maximum elongation; adhesion bond did not fail and specimen did not break.

b Maximum load recorded; specimen did not break.

TABLE 43

SHEAR AND TENSION TEST DATA FOR LP-2 CONTROL COMPOUND NO. 30171-1

Temp., °F	80		-65		180	
			Specimen Size			
Thickness, in.	0.133	0.134	0.133	0.132	0.133	0.133
Width (L_1), in.	0.483	0.485	0.477	0.480	0.485	0.484
Gage length, in.	0.25	0.25	0.25	0.25	0.25	0.25
Area, sq/in.	0.064	0.064	0.063	0.063	0.064	0.064
Length @ failure, in.	1.25	1.05	0.65	0.65	0.65	0.70
			Physical Properties			
Elongation for initial failure, %	400	320	160	160	160	180
Load (P) @ initial failure, lb.	14	14	136	115	5	3
Modulus of stretch @ initial failure						
$\frac{P/L_1 \times 100}{\%\ \text{Elong.}}$, lb/in.	7	9	178	150	6.5	3.5
Type of failure	Co-hesive	Co-hesive	Co-hesive	Ad-hesive	Co-hesive	Co-hesive

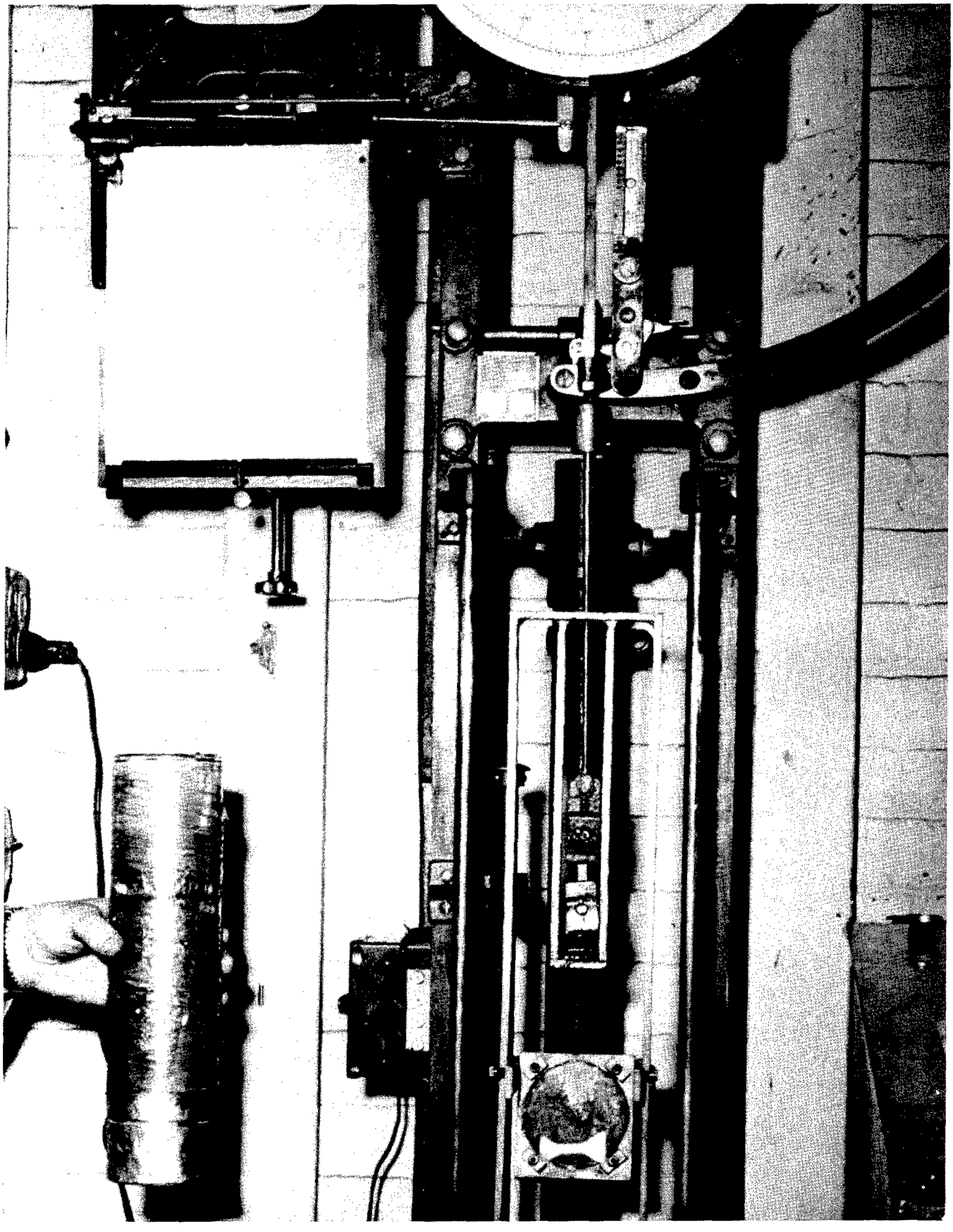
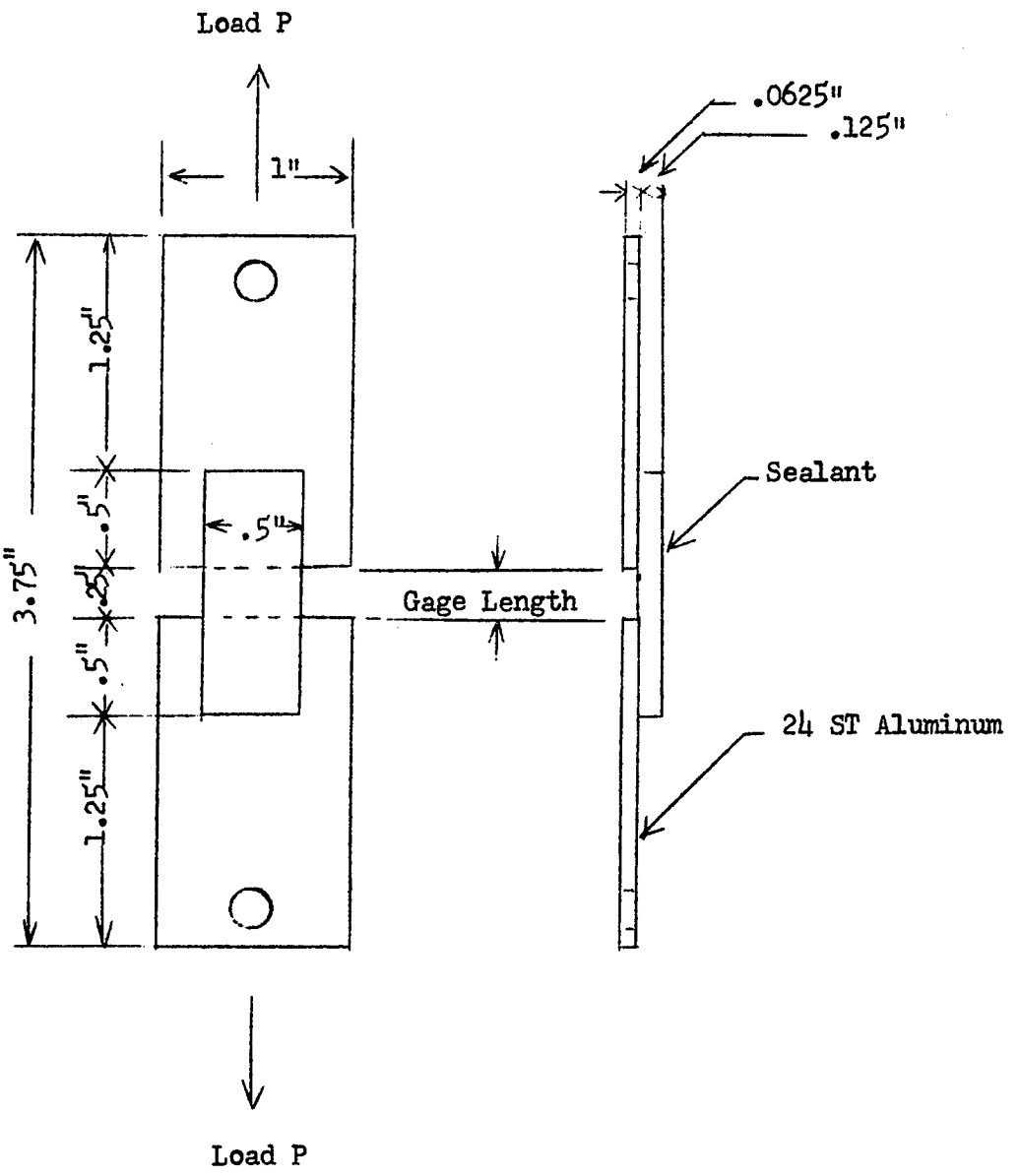


FIG. 20 - TEST JIG FOR STRESS-STRAIN AT VARIOUS TEMPERATURES

FIGURE 21

TEST SPECIMENS USED FOR SHEAR AND TENSION TEST -- CONCENTRATED STRESS



APPENDIX C

GLOSSARY OF TERMS

1. 'Thiokol' WD-2 latex -- A 50% water dispersion of polysulfide polymer with a composition of 99.5 mole % formal and 0.5 mole % trichloropropane. The average particle size is 8 to 15 microns.

2. 'Thiokol' softened WD-2 latex -- WD-2 latex in which the average molecular weight of the polymer has been reduced.

3. 'Thiokol' LP-2 -- A polysulfide liquid polymer with a molecular weight of approximately 4000 and 2.25 rank containing 98 mole % of formal and 2 mole % of trichloropropane cross-linking agent.

4. 'Thiokol' LP-33 -- A polysulfide liquid polymer with an approximate molecular weight of 1000 and 2.25 rank containing 99.5 mole % of formal and 0.5 mole % of trichloropropane.

5. 'Thiokol' ZL-109 -- A polyfunctional mercaptan with an approximate molecular weight of 500 and a rank of 2.25 containing 98 mole % of formal and 2 mole % of trichloropropane.

6. 'Thiokol' ZL-158 -- A polysulfide liquid polymer with an approximate molecular weight of 4500 and 2.25 rank containing 99.5 mole % of formal and 0.5 mole % of trichloropropane.

7. 'Thiokol' ZL-152 -- Formal liquid polymer with a rank of 2.25 and an approximate molecular weight of 4000; no crosslinking agent.

8. Epoxide type resins:

   Epon RN-45 -- Shell Chemical Corporation
   Epon RN-48 -- " " "
   BRR-18794 -- (Modified phenolic resin containing some epoxide polymer) -- Bakelite Corporation
   Pylene PC-2 -- Polymer Industries, Incorporated
   Pylene PC-10 -- " " "

9. Adhesion additives:

   Maleic anhydride
   Furoic acid

10. JP-3A Jet Fuel Specifications:

Gravity, ^{o}API	49.0
Reid Vapor Pressure, p.s.i.	4.0
Freezing Point, ^{o}F	below 76

Accel. gum, mg./100 ml.	6.3
Residue Air Jet, mg./100 ml.	6.1
Copper Strip Corrosion	Pass.
Bromine no.	1.5
Aromatics, % vol.	25
Sulfur, % wt.	0.11
Mercaptan Sulfur, % wt.	0.006
Neutralization No., mg. KOH/gm. sample	0.08
A.S.T.M. Distillation, °F	
IBP	100
5% Rec.	150
10% "	179
20% "	245
30% "	283
40% "	317
50% "	339
60% "	358
70% "	382
80% "	410
90% "	461
E. P.	523
Recovery, %	98.0
Residue, %	1.0
Loss, %	1.0

11. SR-10 fuel -- Diisobutylene.
SR-6 -- Diisobutylene containing 40% aromatics.

12. Rank -- The number represented by x in the polysulfide formula, Na_2S_x.

13. Splitting -- Lowering of polymer molecular weight or chain length by reduction of disulfide bonds with sodium sulfhydrate.

14. Stripping -- Removal of sulfur in excess of disulfide from polymer chains. Polymers can be stripped to rank 2.00.

15. Redistribution -- Disulfide interchange.

16. Toughening -- Increasing polymer molecular weight by removal of low molecular weight fragments.

17. Formal -- bis (2-chloroethoxy) methane; bis (2-chloroethyl) formal.

18. Cake hardness -- Shore A hardness of the latex polymer cake.